VOL. XVIII. DECEMBER, 1896. NO. 10.

AMERICAN CHEMICAL JOURNAL.

INVESTIGATIONS ON THE TWO ISOMERIC CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

BY IRA REMSEN.

In earlier articles[1] the preparation and general properties of the two isomeric chlorides of orthosulphobenzoic acid were described, and evidence was presented which clearly shows that the chloride melting at the higher temperature (76°) has the symmetrical structure represented by the formula $C_6H_4<^{COCl}_{SO_2Cl}$. There was, however, very little direct evidence available bearing upon the structure of the chloride melting at 21.5°–22.5°, and, although it seemed highly probable that it has the unsymmetrical structure represented by the formula $C_6H_4<^{CCl_2}_{SO_2}>O$, this view lacked a firm experimental basis. Work upon the two chlorides has been continued since the articles referred to were published, and a number of facts of interest have been established. The only piece of evidence bearing upon the structure of the low-melting chloride is that furnished by the action of ammonia upon it. Experiments described below show that the observation first made by A. D. Chambers in this laboratory that ammonia converts the low-melting chloride into the ammo-

[1] This JOURNAL, 17, 309, 311, 330, 347.

nium salt of orthocyanbenzenesulphonic acid is correct, while it has repeatedly been shown that ammonia converts the symmetrical or high-melting chloride into the ammonium salt of benzoic sulphinide (saccharin). The two reactions are, therefore, to be represented by the following equations:

I. $C_6H_4<\begin{matrix}COCl\\SO_2Cl\end{matrix} + 4NH_3 = C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N.NH_4 + 2NH_4Cl.$

Symmetrical chloride. Ammonium salt of benzoic sulphinide.

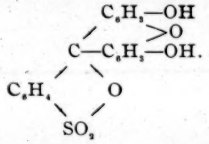
II. $C_6H_4<\begin{matrix}CCl_2\\SO_2\end{matrix}>O + 4NH_3 = C_6H_4<\begin{matrix}CN\\SO_3NH_4\end{matrix} + 2NH_4Cl.$

Unsymmetrical chloride. Ammonium orthocyanbenzenesulphonate.

While the latter equation represents the principal action of ammonia upon the unsymmetrical chloride when proper precautions are taken, it does not represent all that takes place, for the ammonium salt of benzoic sulphinide is always formed to some extent. This appears to be due to a partial transformation of the unsymmetrical in the symmetrical chloride in the presence of aqueous ammonia.

In some of the experiments described below great precautions were taken to purify the two chlorides, and it is believed that the products obtained and described are individuals, each free from its isomer. Starting with these pure substances the action of various reagents upon them was carefully studied. While with ammonia, aniline, and the toluidines they give isomeric products, with water, phenols, and benzene, in the presence of aluminium chloride, both yield the same products, which are in some cases those corresponding to the symmetrical arrangement, and in others those corresponding to the unsymmetrical arrangement. Thus, with water, both give orthosulphobenzoic acid, the reaction taking place more readily with the unsymmetrical than with the symmetrical chloride. With ordinary phenol both yield the symmetrical product, the diphenyl ether of orthosulphobenzoic acid $C_6H_4<\begin{matrix}COOC_6H_5\\SO_2OC_6H_5\end{matrix}$. On the other hand, with resorcinol both yield sulphonfluoresceïn, which, in all probability, considering its close resemblance to ordinary fluoresceïn, has

the unsymmetrical structure represented by the formula



As has been shown by Saunders and myself,[1] the symmetrical chloride gives first the chloride, $C_6H_4<\begin{matrix}COC_6H_5\\SO_2Cl\end{matrix}$, and then orthobenzoyldiphenylsulphone, $C_6H_4<\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$, when treated with benzene in the presence of aluminium chloride. It has now been found that the product of the action of benzene and aluminium chloride on the low-melting or unsymmetrical chloride is orthobenzoyldiphenylsulphone, as in the case of the symmetrical chloride.

Obviously, the careful study of this peculiar case is of interest from the point of view of the hypothesis of tautomerism. Here we have the two definite isomeric substances in crystallized form and with characteristic properties. Both have been purified so that repeated recrystallizations effect no change in the crystalline form or in the melting-points, and yet these two substances act in what appears to be an entirely irresponsible way, making it impossible to predict in any unstudied case whether a symmetrical or an unsymmetrical product will be formed. Further, one of these chlorides does not pass over into the other under any ordinary circumstances—certainly not under the influence of heat. As will be seen, special experiments were undertaken in the hope of effecting such transformation, but without success.

The relations of the two anilides derived from the two chlorides have been investigated and methods devised for the transformation of one into the other. The reactions studied are of such a character as to leave no room for doubt that the two anilides are what they were supposed to be when the first articles on this subject were written, that is to say, one is the

[1] This JOURNAL, 17, 347.

normal symmetrical anilide, $C_6H_4<\begin{matrix}CONH.C_6H_5\\SO_2NH.C_6H_5\end{matrix}$, while the other is the unsymmetrical anilide, $C_6H_4<\begin{matrix}C(NHC_6H_5)_2\\SO_2\end{matrix}>O$. Both are converted into the dianil of the formula,

$$C_6H_4<\begin{matrix}C=N.C_6H_5\\SO_2\end{matrix}>N.C_6H_5,$$

by phosphorus oxychloride and by phosphoric anhydride; and the same product is formed by the action of phosphorus pentachloride on the infusible or unsymmetrical anilide. When the dianil is boiled with glacial acetic acid or with alcoholic potash the unsymmetrical anilide is formed from it. Other transformations of these anilides will be described which go to show that they are closely related substances, both containing two aniline residues.

IV.—PURIFICATION OF THE CHLORIDES, AND ACTION OF VARIOUS REAGENTS UPON THEM.

By Ira Remsen and S. R. McKee.

In the preparation of the mixture of the two chlorides by the action of phosphorus pentachloride upon the acid potassium salt of orthosulphobenzoic acid, certain material improvements have been introduced by which the yield is increased to about 95 per cent. The process as now carried out is as follows:

The acid potassium salt, in quantities of 75–100 grams, is placed in a porcelain dish with $2\frac{1}{2}$ molecules phosphorus pentachloride, and rubbed with a pestle until the action is over, when the whole mass is liquid. This liquid mass is then transferred to a flask, and the phosphorus oxychloride distilled off under diminished pressure. In this operation a small quantity of phosphorus pentachloride collects in the tube, showing that it is present in slight excess. The oxychloride may be evaporated off, as in the former method, by heating the dish on a water-bath for about three hours, if it is preferred, as the yield was practically the same in both cases. When the oxychloride is driven off the mass is trans-

ferred to a tall glass cylinder, containing 200–250 cc. of water and washed by vigorously churning it with a glass rod terminating in a ring. After two or three washings it was poured into a beaker and placed in a freezing-mixture, when it soon became completely solid. To prevent the formation of a solid cake and also to facilitate the freezing, it should be stirred and broken up with a spatula. It is then thoroughly ground up in a mortar with ice-water, transferred to a filter, and washed with ice-water, with the aid of a pump. In this way the chlorides can be freed from potassium chloride and phosphorus compounds. After drying as far as possible with the pump, the mass can be further dried by placing it between layers of drying-paper, and pressing with a plate, or rolling a glass rod over it. Care must be taken, however, not to touch it with the hands, or anything that is warm. If the mass is now placed in a beaker, and kept in a desiccator over calcium chloride, in a cool place, it remains a dry solid, and can be handled very easily. The wash-water should be evaporated, for the purpose of recovering a small quantity of the acid potassium salt it contains.

Several experiments were made to see if the chlorides could with advantage be extracted with ether after distilling off the phosphorus oxychloride, but no distinct advantage was gained. In two cases, however, when 2 molecules of phosphorus pentachloride was used and the chlorides extracted with ether, crystals of another substance were deposited in small quantity from the ether extract, before the chlorides separated. These were thought to be the anhydride of orthosulphobenzoic acid, $C_6H_4 <^{CO}_{SO_2}> O$, and an investigation by Mr. Sohon, of this laboratory, has proved that the assumption was correct, and that the substance is formed in large amount when a smaller quantity of phosphorus is used.

Separation of the Two Chlorides.

1. The Pure High-melting Chloride.—Heretofore this substance has been obtained by dissolving the mixed chlorides in chloroform, shaking this solution with ammonia, separating the chloroform solution, and evaporating. Ammonia acts

much more easily on the low-melting than on the high-melting chloride, and thus it is possible to get rid of the former.

Shaking the mixed chlorides with aqueous ammonia was tried, and it was found that nearly all the low-melting constituent could be destroyed in this way. By repeating this several times, and then crystallizing from ligroïn, the high-melting chloride can be prepared in pure condition. This substance melts, according to Remsen and Saunders,[1] at 76°–77° (uncorr.), but a product has been obtained by the above method, which melts somewhat higher. A portion melting at 76°–77° was alternately shaken with dilute ammonia, and crystallized from ligroïn (boiling-point 90°–125°) nine times. The melting-point gradually rose until the sixth crystallization, when it was 79°–79°.5 (uncorr.); but after that there was no further rise. The thermometer used was correct for the boiling-point of water.

It has been found that when the mixed chlorides are dissolved in ether, shaken with dilute ammonia, and the solution in ether evaporated, the high-melting chloride can be obtained very easily. So that the best method, and the one now used, is to shake the mixed chlorides with dilute aqueous ammonia until nearly all the low-melting constituent is destroyed; then dissolve in ether, cool down to about 0° by adding ice, and shake with dilute ammonia. The ether solution is separated, dried over calcium chloride, and most of the ether distilled off. From the residue good crystals of the chloride, melting at 79°–79°.5, are obtained.

2. The Pure Low-melting Chloride.—By fractional crystallization of the mixed chlorides from petroleum ether in the cold, Remsen and Saunders[2] obtained a small quantity of the low-melting chloride in pure condition (melting-point 21°.5–22°.5.) After various attempts to effect a separation of the two chlorides during the past year, a method has been devised which gives satisfactory results, though it is somewhat tedious. It is as follows: A portion of the mixed chlorides is dissolved in absolute ether, placed in a cool place, and allowed to stand for about a day, when nearly all of the ether will have evaporated, and there will be a separation of crystals of

[1] This JOURNAL, 17, 347. [2] *Loc. cit.*

the high-melting chloride. The oily portion, consisting mainly of the low-melting chloride, is drained off and dissolved in ligroïn (boiling-point 90°–125°). This solution is placed in an Erlenmeyer flask, and a current of dry air drawn through the flask. The liquid must be kept cold, however, or else the substance will not crystallize; and for this purpose a refrigerating-box was devised. This is made of galvanized iron, and consists of an outer and an inner chamber, with a space of about four inches between them. The outer chamber has a cover, and is surrounded by a thick layer of cotton. When this is filled with broken ice the temperature of the inner chamber can be kept at 0° for several days. The flask containing the solution is placed in the inner chamber, and this covered with cotton, or a piece of asbestos board with small holes cut in it for the passage of the glass tubes leading into the flask. The air is dried with sulphuric acid and calcium chloride. After a time two kinds of crystals are noticed, stout columns and radiating tufts of fine needles. The columns melt at 70°–75°, and the needles at 22°–23° (uncorr.) As a rule the columns do not appear until some time after crystallization begins, owing to the fact that part of the high-melting chloride has already been removed by crystallization from ether. When evaporation has proceeded far enough, the mother-liquor is poured off, and the columns removed with a properly constructed spatula. If this is done carefully, very little is left except the radiating tufts. These are then redissolved in ligroïn and the process repeated. Sometimes the columns are observed in the second crystallization, if the solution is evaporated far enough; if so, they are removed as before. As a rule the substance was recrystallized twice after columns ceased to appear, and all the low-melting chloride used in the experiments, hereafter described, was thus treated. After the final crystallization, the mother-liquor should be washed out with cold ligroïn, and the crystals removed and dried. The crystals thus obtained melted at 21°.5–22°.5 (uncorr.), and the melting-point was not lowered by recrystallization. In no case should the solution of the chlorides be saturated, even at 0°, for the solution then becomes cloudy, and the substance does not crystallize so well.

When the high-melting chloride is removed, it is best, in all crystallizations, to add three or four individual crystals of the low-melting chloride when crystallization is just about to begin, for without this, in some cases, only an oil is obtained.

Petroleum ether of different boiling-points was tried, but nothing gave as satisfactory results as ligroïn, boiling-point 90°–125°. Moreover, it was found necessary to purify the commercial ligroïn, as the chlorides absorb something from it and become darkened in consequence. It was shaken in a large separating-funnel with strong sulphuric acid until it almost ceased to color the acid, washed with hot water, then with a hot, dilute solution of sodium hydroxide, then with hot water until free from alkali; then dried over calcium chloride, and filtered.

Action of Water on the Pure Chlorides.

Remsen and Saunders[1] showed that both of the pure chlorides are decomposed by water, yielding orthosulphobenzoic and hydrochloric acid, but noted no difference in the rate of action. The following experiment shows that there is a difference, and that the low-melting chloride is acted on by water about three times as rapidly as the high-melting. 0.8 gram of each of the chlorides was placed in a small flask, and 50 cc. of water added. The flasks were shaken and placed aside. Every twenty-four hours 10 cc. of the water was removed and titrated with silver nitrate and 10 cc. of pure water added. The results were as follows:

	Pure high-melting chloride. Decomposition.		Pure low-melting chloride. Decomposition.	
	Daily.	Total.	Daily.	Total.
1	3.96	3.96	11.87	11.87
2	5.66	9.60	21.30	32.20
3	5.48	15.08	17.77	50.78
4	4.71	19.80	14.08	64.91

Action of Phenol.

By heating the high-melting chlorides and the mixed chlorides with phenol, Remsen and Saunders[2] obtained the normal diphenyl ether of orthosulphobenzoic acid, $C_6H_4<\begin{matrix}CO.OC_6H_5\\SO_2.OC_6H_5\end{matrix}$, and a red substance which was not investigated. The work

[1] *Loc. cit.* [2] *Loc. cit.*

was repeated, and the diphenyl ether obtained, but no considerable amount of the red-colored substance, although special efforts were made to get it. After the action was over, instead of treating with sodium hydroxide, ammonia was added. The whole mass at once became oily, and, on standing for some time, solid. From this a new substance was obtained, as will be shown below. The action of phenol was tried at various temperatures, ranging from 40° to 120°, but the temperatures at which the largest yields and the cleanest products were obtained was 40°–45°. In every experiment with phenol the red color was observed, even with the purest specimens of the chlorides.

1. *Action on the High-melting Chloride.*—5 grams of the chloride (melting-point 79°-79°.5), was heated with 4 grams (2 molecules) phenol for five hours at 40°–45°, and then dilute ammonia added. After stirring for some time the oily mass became solid; it was then filtered, washed, and dried. The yield was 4.175 grams. This, when crystallized from alcohol, gave the diphenyl ether and the new substance described below.

Phenyl Orthosulphaminebenzoate.—When the solid substance, obtained above, was dissolved in alcohol, water added slowly till crystallization was just about to begin, and the solution then allowed to cool slowly, crystals of the diphenyl ether (melting-point 117°–118°) separated. After filtering, the mother-liquor was evaporated and a little more water added, when it became cloudy. On cooling slowly, feathery crystals separated, which melted at 128°–130°, and on crystallization melted quite sharply at 131°–132° (uncorr.). This substance proved to be an amide of the formula $C_6H_4<^{CO.OC_6H_5}_{SO_2NH_2}$, formed by the following reactions:

$$C_6H_4<^{COCl}_{SO_2Cl} + HOC_6H_5 = C_6H_4<^{CO.OC_6H_5}_{SO_2Cl} + HCl;$$

$$C_6H_4<^{CO.OC_6H_5}_{SO_2Cl} + NH_3 = C_6H_4<^{CO.OC_6H_5}_{SO_2NH_2} + HCl.$$

The analyses were as follows:

I. 0.1527 gram gave 0.1241 gram $BaSO_4$ (Carius method).

II. 0.1532 gram gave 0.1251 gram $BaSO_4$ (Carius method).

III. 0.314 gram gave 0.01637 gram nitrogen (absolute method).

	Calculated for $C_{13}H_{11}SO_4N$.	Found. I.	II.	III.
S	11.55	11.16	11.22	....
N	5.05	....	....	5.21

The second sulphur determination was made by Mr. Ragland, and the nitrogen determination by Mr. Mackay, of this laboratory.

The intermediate product could not be isolated. Several attempts were made to get the corresponding acid by boiling with water after the action was over, and also to prepare the anilide, but these were unsuccessful; only orthosulphobenzoic acid and the fusible and infusible anilides could be obtained. The presence of the phenol complicated matters very much, and besides, the action of phenol on the original chloride could never be made complete.

At higher temperatures the yield of the phenyl orthosulphaminebenzoate was smaller, though a small quantity was obtained even at 100°. It seems, then, very probable that part of the action, at least, gives an intermediate product, and that at a higher temperature the action goes to the full extent. The diphenyl ether, however, is formed at the lowest temperature at which the action takes place; at 40°–45° about equal quantities of each are formed.

2. *Action on the Mixed Chlorides.*—When the mixed chlorides were used, the same two substances were obtained, though there was proportionally a somewhat smaller yield of phenyl orthosulphaminebenzoate.

3. *Action on the Low-melting Chloride.*—2 grams of the low-melting chloride was heated with 1.6 grams phenol for five hours, at 40°–45°, and the product treated as above. Both substances were obtained and in approximately equal quantities. It was hoped that an isomeric substance would be formed, but there was not the slightest indication of this.

Decomposition of the Diphenyl Ether.

1. *Decomposition with Ammonia.*—The diphenyl ether is not acted on by strong ammonia under ordinary pressure, even

when boiled. When heated in a sealed tube for two hours at the temperature of the water-bath, the action is very slight, but, when heated in a sealed tube at 125° for four hours, the decomposition is complete. There is formed a dark-colored solution, which gives off phenol when heated. By heating with water all the phenol can be driven off, and on evaporating to a small bulk, crystals of a sweet-tasting substance separate. When these are dissolved in water and the solution acidified, there is a large deposit of benzoic sulphinide. The substance formed is the ammonium salt of the sulphinide, $C_6H_4<\overset{CO}{SO_2}>N.NH_4$, and the reaction is, in all probability, to be represented thus:

$$C_6H_4<\overset{CO.OC_6H_5}{SO_2.OC_6H_5} + 2NH_3 = C_6H_4<\overset{CO}{SO_2}>N.NH_4 + 2C_6H_5OH.$$

2. *Decomposition with Hydrochloric Acid.*—Portions of the diphenyl ether were heated with concentrated hydrochloric acid in a sealed tube, at 100°, at 125°, and at 150° for several hours without action. When, however, it was heated to 200° for six hours, there was complete decomposition. The dark-colored liquid, when evaporated, gave a strong odor of phenol, and when the phenol was all driven off, the solution was evaporated to dryness to expel the hydrochloric acid. The solid residue, when dissolved in water, gave a strong acid reaction. The solution was neutralized with barium carbonate, boiled with animal charcoal, and evaporated. Good crystals were obtained, answering to the description of the neutral barium salt of orthosulphobenzoic acid made and described by Remsen and Dohme.[1]

I. 0.3394 gram when heated lost 0.0328 gram water.

II. 0.3394 gram gave 0.212 gram $BaSO_4$.

	Calculated for $C_7H_4SO_5Ba + 2H_2O$.	Found.
H_2O	9.65	9.66
Ba	36.72	36.74

3. *Decomposition with Potassium Hydroxide.*—A portion of the diphenyl ether was heated for some time on a water-bath

[1] This JOURNAL, 11, 332.

with a moderately concentrated solution of potassium hydroxide, but as there seemed to be no action, it was boiled for about twenty minutes. Still there was no action, as was shown by filtering and evaporating the filtrate. When treated with alcoholic potash, however, and heated, the whole went into solution, and almost immediately there was a deposit of fine needles. The odor of phenol was also very pronounced, when the filtrate was acidified. The substance was recrystallized from alcohol and analyzed. In appearance the crystals corresponded to the neutral potassium salt of orthosulphobenzoic acid, made and described by Remsen and Dohme.[1]

I. 0.220 gram heated at 185° lost in weight 0.0181 gram.

II. 0.220 gram gave 0.1255 gram K_2SO_4.

	Calculated for $C_7H_4SO_5K_2 + 1\frac{1}{2}H_2O$.	Found.
H_2O	8.86	8.23
K	23.57	25.55

Action of Resorcinol.

1. *Action on the High-melting Chloride.*—A portion of the pure high-melting chloride was heated with resorcinol (2 molecules) for four hours, at 75°–80°, the action taking place readily at that temperature. The whole mass became soft, and hydrochloric acid was given off freely. At the end of this time it had become quite stiff. The temperature was then raised to 90°, and the heating continued about two hours longer. The evolution of hydrochloric acid had about ceased, and the mass had become quite hard. On adding sodium hydroxide, the whole went into solution. This solution was very dark-colored, but, on distilling, it gave a beautiful fluorescence, and on adding acid a yellowish-brown mass was precipitated. This was redissolved, heated with animal charcoal, filtered and precipitated by acid, when the color became brownish yellow. It was dried in the air on a plate, and then in a desiccator. A portion was heated at 125°–130° for three hours, but lost no water.

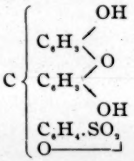
I. 0.1467 gram gave 0.329 gram CO_2 and 0.0498 gram H_2O.
II. 0.1509 " " 0.338 " " " 0.0506 " "
III 0.1553 " " 0.0948 " $BaSO_4$ (Carius method).

[1] *Loc. cit.*

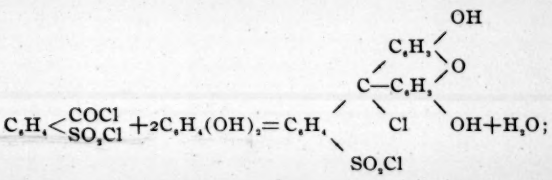
	Calculated for $C_{13}H_{12}O_6S$.	Found. I.	II.	III.
C	61.96	61.16	61.09	...
H	3.26	3.77	3.73	...
S	8.70	...	...	8.39

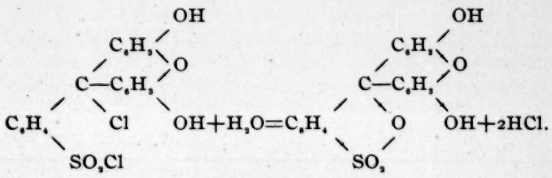
The combustions were made by the lead chromate method as modified by DeRoode,[1] but it was found necessary to mix the substance with potassium bichromate in a boat, to burn it. Sulphonfluoresceïn dried in the air contains a molecule of water which it gives off at 125°–130°. The specimen analyzed in this case was dried in a desiccator.

Assuming that this fluoresceïn is analogous to the ordinary fluoresceïns the formula is :



The formation of this substance from the symmetrical chloride can be accounted for in this way :





[1] This JOURNAL, 13, 226.

2. *Action on the Low-melting Chloride.*—When the low-melting chloride was heated with resorcinol, at the same temperature, reaction took place in the same way, and when sodium hydroxide was added the whole mass went into solution, just as before, and gave a fluorescent substance. This was precipitated by acids, and acted in every way just as the substance above described.

Action of Aniline.

1. *Action on the High-melting Chloride.*—Remsen and Kohler[1] showed that when the high-melting chloride is treated with aniline only the fusible anilide is obtained. Their work was repeated and confirmed, there being no evidence of the formation of any other substance.

2. *Action on the Low-melting Chloride.*—In accordance with the work of Remsen and Kohler, it was expected that the action of aniline on the pure low-melting chloride would give only the infusible anilide, but the results were different. 0.8 gram of the chloride was dissolved in ether in a small flask, and a dilute ether solution of aniline added slowly, the flask being kept in cold water. Action took place at once. The ether was evaporated off, and the solid residue washed with dilute hydrochloric acid. The residue went into solution in dilute sodium hydroxide, and was precipitated at once as a flocculent mass, on addition of acid. It crystallized from alcohol in fine needles, which melted at 194°–195°, and acted in every way like the fusible anilide. From the wash-water, on evaporation, there was obtained about an equal quantity of crystals of the infusible anilide, melting at 250°–270°, with decomposition. The experiment was repeated, and the flask kept in a freezing-mixture, but with the same results.

1 gram of the chloride was treated with aniline in the presence of water, and the same substance obtained in apparently the same proportions. The only explanation of this seems to be that, in the presence of aniline, there is a partial transformation of the low-melting into the high-melting chloride, as the product used could not have contained more than the merest trace of the high-melting chloride. Further evidence

[1] This JOURNAL, 17, 330.

of a transformation is presented in the section dealing with the action of ammonia.

The thought that the formation of the fusible or symmetrical anilide as well as of the infusible or unsymmetrical anilide is due to the imperfect purification of the low-melting chloride used in the experiment is absolutely not to be considered. Every precaution was taken in the purification, and we assert that as used here the chlorides were pure chemical individuals.

Action of Ammonia.

1. *Action on the High-melting Chloride.*—Remsen and Saunders[1] showed that when ammonia acts on the high-melting chloride it is converted into the ammonium salt of benzoic sulphinide. The following experiments confirm their results and show that nothing else is formed :

3 grams of the chloride was dissolved in ether, cooled to 0° by adding ice, and shaken for some time with very dilute ammonia. The ether solution was dried over calcium chloride and the ether evaporated. From this 2.6 grams of the chloride was recovered unchanged. The water, when evaporated, gave crystals of ammonium chloride, and also of the ammonium salt of benzoic sulphinide. When acidified it gave a small precipitate of benzoic sulphinide. This experiment was repeated and much more concentrated ammonia used. Very little of the chloride was recovered from the ether, but from the water, on evaporation, crystals were obtained as above and in large quantity. These had a sweet taste, and when dissolved in water and acid added, there was a copious precipitate of benzoic sulphinide. There was no evidence of the formation of any other substance.

2. *Action on the Low-melting Chloride.*—The work of Remsen and Saunders, and also that of Chambers, of this laboratory, made it extremely probable that when ammonia acts on the low-melting chloride at low temperatures, the ammonium salt of orthocyanbenzenesulphonic acid, $C_6H_4<^{CN}_{SO_2ONH_4}$, is formed. This substance has been under investigation during the past year by Mr. Karslake, of this labor-

[1] *Loc. cit.*

atory. The following experiments are of interest in this connection. 0.8 gram of the pure chloride was dissolved in ether, the solution cooled to 0°, and very dilute ammonia added. After shaking for some time, the solution being kept at 0°, the water was drawn off and evaporated nearly to dryness. A few crystals separated, and when these were dissolved in water, and acid added, there was after a time a very small precipitate of benzoic sulphinide. The ether solution was dried with calcium chloride and evaporated nearly to dryness. From this crystals were obtained which resembled the high-melting chloride. These melted at 75°–78°, and when heated with water they gave off hydrochloric acid.

The experiment was repeated with 2 grams of the chloride. When the ammonia solution was drawn off, a rapid current of air was passed through it to expel any ether; it was then filtered, evaporated to a small volume, and allowed to stand over night. The next morning there was a good deposit of botryoidal crystals, similar in every way to those obtained by Chambers and by Karslake. The ether solution was dried with calcium chloride and evaporated. From this was obtained 0.54 gram of the pure high-melting chloride (melting-point 79°–80° uncorr.) These experiments show that in the presence of ammonia, the low-melting is partially converted into the high-melting chloride. This transformation also accounts for the small amount of benzoic sulphinide obtained in the first experiment, as the high-melting chloride is slowly acted upon by very dilute ammonia. The difference between this case and that of the action of aniline is this, that aniline acts readily on both chlorides, and hence both the fusible and infusible anilides are formed from the low-melting chloride.

Action of Benzene and Aluminium Chloride.

1. *Action on the High-melting Chloride.*—Remsen and Saunders[1] showed that when benzene and aluminium chloride act on the high-melting or mixed chlorides, at ordinary temperatures, orthobenzoylbenzenesulphone chloride is formed, and that, when the action is continued at higher temperatures, orthobenzoyldiphenylsulphone is formed. Their work was

[1] *Loc. cit.*

repeated, and, under the same conditions, both of the substances just mentioned were obtained. Moreover, the yields were unsatisfactory just as they had observed.

2. *Action on the Low-melting Chloride.*— 3 grams of the chloride was dissolved in about 15 grams of benzene, and 3–4 grams of aluminium chloride added in portions. Reaction took place at once, and was so vigorous that the vessel had to be plunged into cold water to prevent too violent action. In about ten minutes action ceased, but on heating momentarily in a water-bath, at about 60°, action began again. This was repeated at intervals for about fifteen minutes, when all the action seemed to be over, and a dark-colored heavy layer had separated at the bottom. The whole was then poured into warm water containing a little hydrochloric acid. In a short time a yellowish, oily layer separated at the bottom of the dish, and, when the water was poured off, this soon solidified. It was ground in a mortar, and, when washed and dried, weighed 3.6 grams. Some of this was crystallized from alcohol, and then melted at 181°–183°, but on recrystallization it melted at 182°–184° (uncorr.). In every way it agreed with orthobenzoyldiphenylsulphone. In the mass there was also a little orthobenzoylbenzenesulphone chloride, as was shown by extracting with ether and crystallizing. The reaction proceeded very smoothly, and was more satisfactory than in the case of the high-melting chloride.

The experiment was repeated with 2 grams of the chloride, and the temperature kept down to the freezing-point of benzene. The action was not so vigorous as before, and when it was over the benzene solution was poured into cold water. Instead of evaporating from the water, the benzene layer was poured off and quickly evaporated from a watch-glass. A gummy substance remained, but on washing with alcohol, the gum was easily dissolved. The residue, when crystallized from alcohol, melted at 183°–185° (uncorr.). It was hoped that from the low-melting chloride a substance isomeric with orthobenzoyldiphenylsulphone might be obtained, but there was not the slightest indication of the formation of such a substance.

Other Attempts to Effect a Transformation.

1. *By Heat.*—It was hoped that by heating the low-melting chloride it might be possible to change it into the high-melting form. Accordingly, two portions were heated in sealed tubes, the first for seven hours at about 80°, and the second for twelve hours at about 90°. Each of these was then dissolved in ligroïn, and recrystallized, but only crystals of the low-melting chloride could be obtained.

2. *By the Action of Water.*—A portion of the low-melting chloride was shaken in a large test-tube with water for about one-half hour, then dried, dissolved in ligroïn, and crystallized, but there was no evidence of crystals of the high-melting chloride.

Conclusion.

The results of this investigation may be summed up thus:

1. It has been shown that both the chlorides can be obtained in quantity in pure condition.

2. Water and other agents act on the low-melting chloride much more easily than on the high-melting chloride.

3. Phenol gives two products with each of the chlorides, the diphenyl ether $C_6H_4<\begin{matrix}CO.OC_6H_5\\SO_2.OC_6H_5\end{matrix}$, and the chlorphenyl ether, $C_6H_4<\begin{matrix}CO.OC_6H_5\\SO_2Cl\end{matrix}$, but no isomeric product.

4. The diphenyl ether can be decomposed by various agents, but no difference was found in the relations of the two phenol residues to the rest of the compound.

5. Resorcinol gives sulphonfluoresceïn with both chlorides.

6. With aniline the high-melting chloride gives only the fusible anilide, but the low-melting chloride gives both the fusible and infusible anilides. This is accounted for by a partial transformation of the low-melting into the high-melting chloride.

7. Ammonia gives only the ammonium salt of benzoic sulphinide with the high-melting chloride, but the low melting chloride is partly transformed by it into the high-melting form, and partly into ammonium orthocyanbenzenesulphonate, $C_6H_4<\begin{matrix}CN\\SO_2ONH_4\end{matrix}$.

8. Benzene and aluminium chloride give the same product with both of the chlorides.

V.—THE RELATIONS OF THE ANILIDES.

By Ira Remsen and J. R. Hunter.

Preparation of the Two Anilides.

The best method for the preparation of the anilides was found to be that given below :

25 grams of the mixed chlorides are dissolved in absolute ether in a 500 cc. Erlenmeyer flask. 38.6 grams aniline, also in solution in absolute ether, are added slowly to the chlorides, the solution being constantly stirred. The temperature of the solution is to be kept down by placing the flask in cold water. A white precipitate appears as soon as the aniline is added. When the reaction is over, the ether is distilled off on the water-bath. To avoid bumping, as far as possible, the flask should be shaken constantly during the distillation. The yellowish-white residue consists of a mixture of the two anilides and aniline hydrochloride. Sometimes the residue has an oily appearance, and it usually contains a slight excess of aniline. Cold water acidulated with hydrochloric acid is then added, the mass thoroughly stirred, and the whole allowed to stand several hours. This treatment removes the aniline salts, and leaves the mixture of the two anilides. Some of the infusible anilide will be dissolved in the water with the salts of aniline, hence this should be recovered by evaporating the water to a small volume, when the anilide will crystallize out, the aniline hydrochloride remaining in solution. This anilide is frequently colored, but can be purified by boiling with animal charcoal in dilute alkaline solution.

To separate the two anilides the following method is satisfactory : The mixture is dissolved in hot alcohol, and this solution is cooled as rapidly as possible by putting the vessel in cold water. Under these conditions the fusible anilide crystallizes in thin white needles, while the infusible variety always crystallizes in short thick prisms. By rotating the vessel the fusible anilide will be disseminated through the

alcohol, and may be poured off from the infusible prisms which will quickly settle to the bottom.

Under the conditions described above there is usually formed a small amount of the anil, and sometimes a considerable quantity of it appears. Since this is insoluble in a cold, dilute solution of sodium hydroxide, while the anilides are soluble in that reagent, the latter can be readily separated from the former by that means.

If the molecule of alcohol with which the infusible anilide crystallizes from solution in alcohol is undesirable, the crystals should be dissolved in dilute solution of sodium hydroxide, and the solution acidified, when the anilide will crystallize without water or alcohol of crystallization.

Action of Phosphorus Oxychloride on the Anilides.

1. *On the Infusible Anilide.*—Remsen and Kohler[1] observed that phosphorus oxychloride acts on the infusible anilide, but the products were not isolated. The experiment was repeated. To avoid the action of the oxychloride on rubber or cork a small condenser is fitted over the neck of a tubulated retort. In this apparatus the infusible anilide is then boiled with an excess of the oxychloride, until all of the anilide is dissolved. This is attended by liberation of hydrochloric acid, and the solution becomes quite yellow. When the reaction is complete, the excess of the oxychloride is removed by distillation under diminished pressure. There is left in the retort a light-brown, viscous liquid. While still warm the retort is turned about so that this residue is spread over as much surface as possible. Water is then added, and the retort set aside until the brown viscous mass has disappeared. An insoluble, almost white, material remains, which dissolves in hot alcohol, forming a yellow solution. After repeated crystallizations it melts sharply at 189°.5 C. (uncorr.). An analysis of this product gave the following results:

I. 0.2002 gram gave 0.4997 gram CO_2, and 0.078 gram H_2O.

II. 0.2015 gram gave 0.5020 gram CO_2, and 0.0795 gram H_2O.

III. 0.2443 gram gave 0.1645 gram $BaSO_4$.

IV. 0.1683 gram gave 0.1132 gram $BaSO_4$.

[1] This JOURNAL, 17, 343.

	Calculated for $C_{19}H_{14}N_2SO_3$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	68.26	68.07	67.94	...	...	...	...	...
H	4.19	4.33	4.38	...	...	...	...	...
S	9.58	...	...	9.25	9.21	...	...	...
N	8.41	...	...	...	...	8.63	8.61	8.5

The combustions were made by the lead chromate method, as described by DeRoode,[1] the sulphur determinations by the method of Carius, and the nitrogen determinations by the absolute method, excepting the last one (VII), which Mr. E. Mackay, of this laboratory, kindly made for me by the method of Kjeldahl.

Considerable difficulty was experienced in obtaining satisfactory results for carbon, although the appearance and the melting-point of the compound indicated its purity. Afterward a possible explanation was found in the fact that a little of the anil described by Remsen and Coates,[2] was found to result under the conditions of the experiment. Its formation will be explained below.

When pure this compound has a bright lemon-yellow color, and the crystals obtained from alcohol are beautifully formed arborescent plates, very brittle. It is only slightly soluble in ether, or chloroform, but is readily soluble in benzene, glacial acetic acid, and acetone. When crystallized from either of the last two solvents named, monoclinic prisms of great brilliancy are obtained, the faces developed being usually ∞P, $\infty P\bar{\infty}$, oP, P, and $2P\bar{\infty}$.

2. *On the Fusible Anilide.*—This same compound is formed by the action of phosphorus oxychloride on the fusible anilide, the details of the experiment being the same as above given. Some anil is formed in this case also.

Efforts to get a crystallized product from the brown viscous residue, by using various solvents, were unsuccessful. It appears from the following experiments that this residue is really a solution of the yellow product in phosphoric acid. To a small amount of phosphoric acid prepared by adding a very little water to phosphoric anhydride some of the pure yellow product, was added and the mixture heated. A clear solution was effected, having the same consistency and color as the

[1] This JOURNAL, **12**, 226. [2] *Ibid*, **17**, 321.

residue obtained above; and when water was added to this, it acted in much the same way.

On comparing the empirical formula arrived at by analysis of this yellow product with that of the anilide, from which it is derived, the equation,

$$C_{19}H_{16}SO_3N_2 - H_2O = C_{19}H_{14}SO_2N_2,$$

shows their relation. It thus appears that the action of the oxychloride is one of dehydration.

The Action of Phosphorus Pentoxide.

1. *On the Infusible Anilide.*—It seemed reasonable to expect that the same compound would result if either of the anilides should be treated with a strong dehydrating agent. Accordingly, some infusible anilide was mixed with phosphorus pentoxide in a test-tube and then heated for two hours in an air-bath to 130°–150°, the test-tube being closed by a Bunsen valve. The mass had become slightly yellow in color. When cold, water was added to dissolve the phosphoric acid and anhydride, and the portion insoluble in water was found to have the same crystalline form, when deposited from alcohol, and to melt at the same temperature, as the product from the other experiments with phosphorus oxychloride.

2. *On the Fusible Anilide.*—When the fusible anilide is treated with phosphorus pentoxide, as just described, the same yellow compound is formed.

Neither acetyl chloride nor acetic anhydride effect this dehydration of the anilide.

Hoogewerff and Van Dorp[1] have effected the formation of some isoimides by treating dibasic acid derivatives of the general formula, $R<\begin{matrix}CONHR'\\COOH\end{matrix}$, with either acetyl chloride or phosphorus oxychloride, the reaction with the former being represented by the equations,

$$R<\begin{matrix}CONHR'\\COOH\end{matrix} + CH_3COCl = R<\begin{matrix}C(=N-R')\\COOH\end{matrix}OH + CH_3COCl =$$

$$R<\begin{matrix}C=N.R'\\CO\end{matrix}>O + CH_3COOH + HCl.$$

Isoimides.

[1] Rec. Trav. chim., **12**, 12; also **13**, 93.

With the oxychloride of phosphorus the reaction would be similar. In all cases examined R′ was CH_3, C_2H_5, or $CH_2.C_6H_5$, while R was the residue of camphoric and phthalic acids, respectively. Clearly the rôle of the oxychloride in these reactions is the same as that which it plays in the reactions with the anilides, the equation,

$$3C_6H_4\begin{cases}CONHC_6H_5\\SO_2NHC_6H_5\end{cases} + POCl_3 = 3C_6H_4\begin{cases}C=N.N_2H_3\\SO_2\end{cases}N.C_6H_5 + H_3PO_4 + 3HCl,$$

in all probability represents the reaction with the fusible anilide.

3. *Structure of the Compound.*—From the methods of formation already described, especially those involving the use of the fusible anilide, the formula for which may be regarded as established, it follows that the formula

$$C_6H_4\begin{cases}C=N.C_6H_5\\SO_2\end{cases}N.C_6H_5,$$

represents the structure of the new compound. It thus appears to be a dianil of orthosulphobenzoic acid.

Jesurun[1] obtained this same compound by the action of aniline on orthocyanbenzenesulphone chloride. He thinks the first product formed is a benzamidinesulphanilide,

$$C_6H_4\begin{cases}C\begin{cases}=N.C_6H_5\\NH_2\end{cases}\\SO_2NHC_6H_5\end{cases}$$

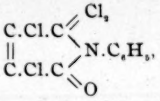
and that this loses ammonia, forming this dianil, to which he gives the above structural formula.

The grouping of the two aniline residues in this dianil is the same as that given by Anschütz and Beavis[2] for dichlormaleïc dianil, the formula of which is,

$$\begin{matrix}C.\ Cl.\ C\\\|\\C.Cl.CO\end{matrix}\begin{matrix}=N.C_6H_5\\\diagdown\\\diagup N.C_6H_5,\end{matrix}$$

[1] Ber. d. chem. Ges., **26**, 2292. [2] *Ibid*, **28**, 58.

which is formed by the action of aniline on dichlormaleïc anil-dichloride,

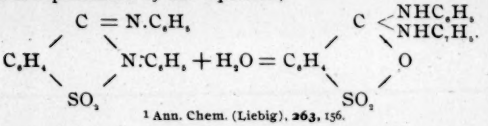


prepared by the action of phosphorus pentachloride on succinanil.[1]

It seems reasonable to expect the formation of analogous derivatives of the anil described by Remsen and Coates. Preliminary experiments have been made with this end in view, but as yet without success. The problem is still under investigation.

4. *Chemical Properties of the Dianil.*—(*a*) It was mentioned above that the compound can be crystallized from glacial acetic acid. For this purpose the solution must not be heated longer than is necessary to effect solution. If the solution is boiled for two or three hours in a flask connected with a reflux condenser, none of the dianil will separate on cooling, but instead, slender, white needles will appear. These are crystals of the infusible anilide. The identity was established by the melting-point, crystalline form when recrystallized from alcohol and from water, ready solubility in dilute cold alkaline solution, from which the characteristic granular crystals of the infusible anilide separate when the solution is acidified. The infusible anilide itself assumes the acicular habit when crystallized from glacial acetic acid. In order further to test the identity some of the needles were treated with phosphorus oxychloride, and the dianil together with some of the ordinary anil was obtained, just as when the granular, infusible anilide was used.

This conversion of the dianil into the infusible anilide is accompanied by a change in color of the acetic acid solution, from a darker to a much lighter shade of yellow. The reaction is represented by the equation,



[1] Ann. Chem. (Liebig), **263**, 156.

The yield is quantitative.

(*b*) The crystals of the dianil can be boiled with a water solution of sodium hydroxide, either dilute or concentrated, without undergoing change. When boiled for about an hour with alcoholic potash it passes into solution. If now the alcohol is evaporated almost completely, no precipitate is formed on addition of water. If, however, the solution is acidified, crystals of the infusible anilide appear on standing, provided the solution is sufficiently dilute. If the solution is quite concentrated, the anilide is precipitated at once by the acid.

The effect of boiling the dianil with alcoholic potash is to cause the dianil to unite with the elements of water and form the infusible anilide. It is worthy of note that these elements arrange themselves in the more stable grouping of the infusible, rather than the fusible anilide, which is less stable.

(*c*) When concentrated hydrochloric acid is added to the dianil the yellow color of the latter changes from yellow to white. If the acid is filtered off at once, and the residue washed with cold water, the yellow color reappears. If, however, the dianil is boiled with the acid for about an hour, the insoluble residue remains white after the acid is completely removed, and when crystallized from alcohol it forms slender, white needles. These are crystals of the anil described by Remsen and Coates.[1] In the hydrochloric acid solution there is some aniline hydrochloride. This reaction is to be represented by the equation,

$$C_6H_4\begin{matrix}C=N.C_6H_5\\ SO_2\end{matrix}N.C_6H_5 + H_2O + HCl = C_6H_4<\begin{matrix}CO\\ SO_2\end{matrix}>N.C_6H_5 + C_6H_5NH_2.HCl.$$

It was mentioned above that some of this anil is always formed during the action of phosphorus oxychloride on the anilides. In the light of the above reaction its presence is explained.

Action of Phosphorus Pentachloride on the Infusible Anilide.

When the infusible anilide is added slowly to a heated solution of phosphorus pentachloride in chloroform, reaction sets in at once, and generally the solution changes to a light

[1] *Loc. cit.*

yellow color. Usually about twice as much of the pentachloride as of the anilide is necessary to effect complete solution of the latter. In the first experiment tried, 2.5 grams of the pentachloride were used to 1 gram of the anilide, and the heating was continued only as long as was necessary to effect complete solution of the anilide. On cooling, radiating tufts of fine, white needles separated, completely filling the liquid. More chloroform was added, and the heat applied till all the needles were dissolved. But the needles did not separate again even when most of the chloroform had evaporated. The last traces of chloroform were then driven off by heating gently for some time, and the yellow, viscous residue was treated as a brown residue from the experiment with the oxychloride. Some of the anil was found present, though the chief product was the yellow dianil. The final products of this reaction are the same as those formed by the action of phosphorus oxychloride on the infusible anilide.

This experiment was repeated under the same conditions as before, and under varied conditions, though always without obtaining the fine white needles. The final products were the same each time.

From the results of these experiments it will readily be seen that it is possible to pass from the fusible anilide to the infusible anilide, by passing first to the yellow dianil and then, by boiling this with glacial acetic acid or an alcoholic solution of potassium hydroxide, to the infusible anilide.

Again, from the dianil one can obtain the anil by boiling with concentrated hydrochloric acid. And since the anil, when boiled with aniline, passes over to the fusible anilide, it is therefore possible to pass in the opposite direction, from the infusible to the fusible anilide.

The Action of Benzoyl Chloride on the Infusible Anilide.

Five grams infusible anilide were boiled with an excess of benzoyl chloride until it dissolved. The excess of the benzoyl chloride was removed as completely as possible by distillation under diminished pressure, and the residue boiled with water. After this water had become cold, and without separating it from the insoluble residue, sodium carbonate

was added to alkaline reaction and the vessel was heated gently on the water-bath to about 60° C. This solution was then poured off from the undissolved residue, and acidified, when benzoic acid was precipitated.

The residue insoluble in sodium carbonate solution was then dissolved in alcohol and boiled with animal charcoal. From this solution plates of a dirty yellow color separated. These, when purified by repeated recrystallization, became white, and assumed the acicular habit, melting sharply at 190°.5 (uncorr.). They proved to be the anil.

The mother-liquor from the above was then evaporated to dryness and the residue boiled with about 750 cc. water, and this water, while still hot, was drawn off from the part insoluble in the water, which had melted to a brown oil. By repeatedly boiling this residue with water almost all of it was finally dissolved. From this water on cooling, a white precipitate was deposited. When crystallized from alcohol, this forms small globular-shaped tufts of white needles, but these have not yet been identified, partly from lack of material, partly from lack of time.

From the water filtrate from this white precipitate, after evaporating to a very small volume, a small quantity of benzanilide was obtained, which was identified by its melting-point, crystal form, and by comparison with a specimen of benzanilide. The equation,

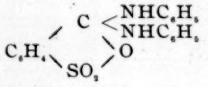
$$C_6H_4\begin{cases} C<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix} \\ SO_2>O \end{cases} + C_6H_5COCl = C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N.C_6H_5 + C_6H_5CONHC_6H_5 + HCl,$$

represents the reaction so far as yet understood.

A second experiment gave the same results as the one just described. No trace of the product mentioned by Remsen and Kohler,[1] as giving rise to the infusible anilide on addition of aniline, was obtained in either case. It is possible that this product might be isolated by keeping the temperature as low as possible during the reaction.

[1] This JOURNAL, 17, 342.

From the results obtained in this investigation it is clear that the two aniline residues are intact in the infusible anilide. This fact, together with the further fact that this anilide is derived only from the liquid, or unsymmetrical, chloride, by the action of aniline, leaves but little if any doubt that the structure of the anilide is correctly represented by the formula,

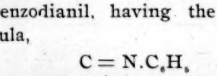


first proposed by Remsen and Coates.[1]

Summary.

The results arrived at in this investigation may be briefly summarized as follows:

1. Orthosulphobenzodianil, having the structure represented by the formula,



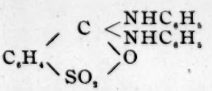
is obtained by the action of phosphorus oxychloride or phosphoric anhydride on either anilide, and by the action of phosphorus pentachloride on the infusible anilide.

2. The infusible anilide is regenerated from this dianil on boiling the latter with glacial acetic acid or with alcoholic potash.

3. The anil of orthosulphobenzoic acid is obtained by boiling this dianil with concentrated hydrochloric acid.

4. Benzoyl chloride acts on the infusible anilide, forming benzanilide and the anil of orthosulphobenzoic acid.

5. The two aniline residues are intact in the infusible anilide, and this anilide has the structure represented by the formula,



[1] *Ibid.*, **17**, 320.

VI.—ORTHOCYANBENZENESULPHONIC ACID.

By Ira Remsen and W. J. Karslake.

The object of the work described below was to investigate the substance first obtained by Chambers in this laboratory as a product of the action of aqueous ammonia on the chlorides of orthosulphobenzoic acid, and supposed to be the ammonium salt of orthocyanbenzenesulphonic acid, $C_6H_4 <^{CN}_{SO_2ONH_4}$, formed from the unsymmetrical chloride, in the same way that the ammonium salt of orthocyanbenzoic acid, $C_6H_4 <^{CN}_{COONH_4}$, is formed from phthalyl chloride, as shown by Hoogewerff and Van Dorp.[1]

Preparation of Ammonium Orthocyanbenzenesulphonic Acid.

As the result of a large number of experiments the following method was finally adopted: 30 grams of the mixed chlorides prepared according to the directions of Remsen and McKee,[2] were dissolved in about 125 cc. ether and placed in a 500 cc. separating-funnel. Finely crushed ice was added and the whole shaken. About 100 cc. of the ice-cold water was now added and then dilute ammonia (1 : 5) in small portions at a time, care being taken to shake thoroughly after each addition until a slight excess remained after shaking for about two minutes. Meantime crushed ice was frequently added so that there was always some present. The water solution was now drawn off, washed once or twice with ether, filtered, and evaporated to crystallization upon the water-bath. 9 grams of impure ammonium orthocyanbenzenesulphonate were obtained, which is a yield of 30 per cent. Generally, however, the yield obtained by this method in later experiments was from 20 to 25 per cent. A word should also be said in regard to the crystallization of solutions from which the ammonium orthocyanbenzenesulphonate is to be obtained. At first the ammoniacal water solution was evaporated upon the water-bath to small bulk, so that, upon cooling, large quantities of ammonium chloride and the ammonium salt of benzoic sulphinide separated out with the ammonium ortho-

[1] Rec. Trav. chim., 11, 84; 12, 12; 13, 13. [2] See p. 794.

cyanbenzenesulphonate. The mass thus obtained, after being drained by the aid of the suction-pump, was treated in a beaker with small quantities of cold water which dissolved the ammonium chloride and the ammonium salt of benzoic sulphinide much more rapidly than it did the compact nodules of the ammonium orthocyanbenzenesulphonate. At its best, however, this is a poor method of separation, although at times, even later, it was found advantageous to resort to it. The method of treating the well-drained and perfectly dry mass with absolute alcohol, filtering from the undissolved ammonium chloride and evaporating to crystallization, was also tried, but did not give satisfactory results. It was found that the best method consists in evaporating the solution to such a concentration that crystallization begins only after the perfectly cold solution has stood for a few hours. It seems that some time is required for the ammonium orthocyanbenzenesulphonate to arrange itself in crystalline form, that it has a tendency to form supersaturated solutions. It was frequently noticed that, if the solution was too concentrated, the ammonium chloride and the ammonium salt of benzoic sulphinide would separate first, while, if the same solution was not so concentrated, the ammonium orthocyanbenzenesulphonate separated first. As thus obtained, however, by the above described methods, the salt is still very impure, being contaminated with a quantity of some chlorine compound from which it is extremely difficult to separate it. Although it was taken for granted that this impurity was ammonium chloride, and, indeed, in many cases there can be no doubt that ammonium chloride was present, still a further study in regard to this point seems desirable in order to find out if *only* ammonium chloride is present. After a large number of experiments it was found that alternate recrystallizations from absolute alcohol and from water furnished the salt in pure condition, although, even by this method, at least 5 or 6 crystallizations were required. Repeated recrystallization from absolute alcohol alone gives good results. As thus obtained the salt crystallizes from alcohol in beautiful transparent needles arranged in rosettes, while from water it separates in botryoidal masses composed of radiating, transparent needles.

It is insoluble in ether and chloroform, very soluble in water and hot alcohol, but much less so in cold alcohol, from which it crystallizes best. Upon comparing some of this salt with some previously obtained by Chambers it was found to be identical with it. Of the crystals,

I. 0.2014 gram gave 0.2376 gram $BaSO_4$ = 16.11 per cent. S.

II. 0.1988 gram gave 25.80 cc. nitrogen at 24° C., and 762.9 mm. = 14.58 per cent. N.

III. 0.2125 gram gave 0.2490 gram $BaSO_4$ = 16.10 per cent. S.

	Calculated for $C_6H_4<^{CN}_{SO_3ONH_4}$		Found. I	II.	III.
$C_7H_8O_3$	140	70.00			
S	32	16.00	16.20	....	16.09
N_2	28	14.00	....	14.58	....
	200	100.00			

Analyses I. and II. are those of Mr. Chambers. The nitrogen was determined by the absolute method and the sulphur by the Carius method.

In several experiments in which solutions were evaporated to crystallization in order to obtain the ammonium orthocyanbenzenesulphonate, large, beautiful, transparent plates separated which became dull and opaque after standing for some time in the air. They were first obtained from a solution of the nearly pure salt which had been put in a desiccator over concentrated sulphuric acid for evaporation and crystallization in the cold. They were again obtained from a solution of 0.8 gram pure salt, which had been dissolved in 20 cc. of water and boiled with a return-condenser for 2½ hours. Lastly, they were obtained, and then in large quantity, upon evaporating the first water solution in order to obtain the first deposit of ammonium orthocyanbenzenesulphonate. The plates were mechanically separated, and dissolved in water for recrystallization. From this solution ammonium orthocyanbenzenesulphonate in its well-known form separated, and not the plates. Of the few plates which were obtained in the first observation analyses were made :

I. 0.4657 gram gave 0.5600 gram $BaSO_4$ = 16.52 per cent. S.
II. 0.4060 gram gave 0.4735 gram $BaSO_4$ = 16.02 per cent. S.

They suffered no loss upon heating to 190° C. The sulphur determinations were made by the Liebig method. Repeated experiments under apparently the same and other conditions were made, in order to obtain enough of the salt for a complete analysis, but the plates were not obtained again.

From these few observations, and from the analyses, it would seem, however, that they were another crystalline form of ammonium orthocyanbenzenesulphonate, but further study upon this point is required.

Sodium Salt, $C_6H_4{<}^{CN}_{SO_2ONa} + H_2O$.—This salt has already been described by Jesurun,[1] who made it by treating orthocyanbenzenesulphone chloride with sodium hydroxide. It is also formed by treating one molecule of the ammonium salt with one molecule of sodium hydroxide and evaporating to crystallization upon the water-bath. It crystallizes from concentrated solutions in large, transparent, prismatic plates containing one molecule of water of crystallization.

Of the crystals,

I. 0.2097 gram gave 0.2227 gram $BaSO_4$ = 14.59 per cent. S.
II. 0.1134 gram gave 0.1193 gram $BaSO_4$ = 14.45 per cent. S.
III. 0.2228 gram gave 0.2372 gram $BaSO_4$ = 14.62 per cent. S.
IV. 0.1920 gram lost 0.0158 gram at 150° = 8.23 per cent. H_2O, and gave 0.0613 gram Na_2SO_4 = 10.34 per cent. Na.

	Calculated for $C_6H_4{<}^{CN}_{SO_2ONa}+H_2O$.		Found.			
			I.	II.	III.	IV.
$C_7H_4NO_3$	150.0	67.27	....	....	....	....
S	32.0	14.35	14.59	14.45	14.62	....
Na	23.0	10.31	....	....	....	10.34
H_2O	18.0	8.07	....	....	....	8.23
	223.0	100.00				

There was no further loss in weight upon heating to 195° C. Analysis I. is that of Mr. Chambers of the salt which he made.

Potassium Salt, $C_6H_4{<}^{CN}_{SO_2OK}$.—This salt is made by treating the ammonium salt with the calculated quantity of

[1] Ber. d. chem. Ges., 26, 2288.

potassium hydroxide. It is much less soluble than the corresponding sodium salt, and crystallizes from moderately dilute solutions in small, transparent needles radiating from a common centre. In habit it is not unlike the ammonium salt. It is very easily prepared. Of the crystals,

I. 0.2128 gram gave 0.0830 gram K_2SO_4=17.61 per cent. K.

II. 0.2295 gram gave 0.0903 gram K_2SO_4=17.66 per cent. K.

III. 0.2550 gram gave 0.2824 gram $BaSO_4$=15.22 per cent. S.

	Calculated for $C_6H_4<^{CN}_{SO_2OK}$.		Found.		
			I.	II.	III.
$C_7H_4NO_2$	150.0				
S	32.0	15.16	....	....	15.22
K	39.1	17.67	17.61	17.66	....
	221.1				

The salt lost nothing in weight when heated to 190° C.

Barium Salt, $\left(C_6H_4<^{CN}_{SO_2}\right)_2 Ba + 2H_2O$. — Considerable difficulty was experienced in preparing this salt. There seemed to be a strong tendency on the part of the nitrile group to undergo saponification, thus giving rise to the formation of mixtures. The analyses given below are of some crystals which were used in the attempt to prepare the free acid. These were obtained by treating the ammonium salt with only three-fourths of the calculated quantity of barium hydroxide, and gently heating upon the water-bath until no more ammonia was given off. It was then filtered, evaporated to small bulk, and crystallized from dilute alcohol. It separated in little tufts composed of white silky needles. They were washed with alcohol to free them from any of the ammonium salt which might be present. Of the air-dried crystals,

I. 0.1065 gram gave 0.0459 gram $BaSO_4$ = 25.37 per cent. Ba.

II. 0.1882 gram gave 0.0812 gram $BaSO_4$ = 25.56 per cent. Ba.

III. 0.1006 gram lost 0.0070 gram at 135° C = 6.96 per cent. H_2O, and gave 0.0438 gram $BaSO_4$ = 25.59 per cent. Ba.

	Calculated for $(C_6H_4{<}^{CN}_{SO_3})_2Ba+2H_2O$.		Found. I.	Found. II.	Found. III.
$C_{14}H_8N_2O_6$	300.0	....	....	....	....
Ba	137.0	25.51	25.34	25.36	25.59
$2H_2O$	36.0	6.71	....	....	6.96
	473.0				

As stated above, this salt was used in the attempt to prepare free orthocyanbenzenesulphonic acid. It was dissolved in water, and dilute sulphuric acid carefully added until no further precipitation of barium sulphate took place. It was then filtered, evaporated to a small bulk on the water-bath, and placed in a desiccator over sulphuric acid. A syrupy, transparent mass was obtained, which slowly solidified into very fine needles arranged in rosettes. These were then washed with ether containing a little alcohol, and finally with ether alone. They melted at 181°–182° uncorrected. Of the crystals,

0.1880 gram gave 0.2037 gram $BaSO_4$ = 14.91 per cent. S.

The formulas, $C_6H_4{<}^{CN}_{SO_3OH}+2H_2O$,

$C_6H_4{<}^{CONH_2}_{SO_3OH}+H_2O$, and

$C_6H_4{<}^{COONH_4}_{SO_3OH}$,

all agree for 14.62 per cent. S by theory. Upon comparison, however, of its melting-point and method of crystallization with the orthobenzaminesulphonic acid described by Fahlberg and Barge,[1] and by Jesurun,[2] there can be little doubt of the identity of the two substances. Therefore its formula is probably

$$C_6H_4{<}^{CONH_2}_{SO_3OH}+H_2O.$$

Not enough of the salt was obtained for a water determination. Other attempts were made to isolate the free acid by other methods but without success. Jesurun also failed to isolate it.

[1] Ber. d. chem. Ges., **22**, 759. [2] *Loc. cit.*

Transformation of Orthocyanbenzenesulphonic Acid into Orthobenzaminesulphonic Acid.

This transformation is most easily effected by boiling with excess of dilute alkalies. Hence it is, that in the preparation of the above described cyan salts, it is essential that not more than the calculated quantity of base should be used. In most cases thereaction proceeds in a normal manner according to the following equation:

$$C_6H_4<\begin{matrix}CN\\SO_2OH\end{matrix} + H_2O = C_6H_4<\begin{matrix}CONH_2\\SO_2OH\end{matrix},$$

and there stops, no further hydrolysis taking place to produce the corresponding ammonium salt as here represented:

$$C_6H_4<\begin{matrix}CONH_2\\SO_2OH\end{matrix} + H_2O = C_6H_4<\begin{matrix}COONH_4\\SO_2OH\end{matrix}.$$

Few salts, however, were obtained, to which no formulas could be assigned.

Ammonium Salt, $C_6H_4<\begin{matrix}CONH_2\\SO_2ONH_4\end{matrix}$.—This salt has already been prepared by Fahlberg and Barge,[1] and described as crystallizing from alcohol in white needles which melt at 255°–256°. Jesurun[2] described it later as crystallizing from water in granular crystals containing 1 molecule of water of crystallization. These descriptions do not agree with the salt we obtained by boiling 3 grams of ammonium orthocyanbenzenesulphonate with dilute hydrochloric acid for eight hours with a return-condenser. On evaporating to dryness on the water-bath several times to drive off most of the hydrochloric acid, there were obtained, by crystallization from a water solution, thin, transparent needles which contained no water of crystallization and melted at 219°–220° uncorr. A sulphur determination was made by the Liebig method. Of the crystals,

0.1918 gram gave 0.2058 gram $BaSO_4$ = 14.74 per cent. S.

The formula $C_6H_4<\begin{matrix}CONH_2\\SO_2ONH_4\end{matrix}$ requires 14.68 per cent. S.

Potassium Salt, $C_6H_4<\begin{matrix}CONH_2\\SO_2OK\end{matrix} + H_2O$.—This salt was made by boiling, with a return-condenser, 3 grams of the am-

[1] *Loc. cit.* [2] *Loc. cit.*

monium cyan salt with excess (3.5 grams) of dilute potassium hydroxide for five hours.

From a moderately concentrated solution there separated transparent, monoclinic (?) prisms, which were once recrystallized from water. Of these crystals,

I. 0.2409 gram lost 0.0169 gram below 135° = 7.01 per cent. H_2O.

II. 0.1727 gram lost 0.0119 gram below 135° = 6.88 per cent. H_2O, and gave 0.0588 gram K_2SO_4 = 15.28 per cent. K.

III. 0.1103 gram gave 0.0376 gram K_2SO_4 = 15.32 per cent.

	Calculated for $C_6H_4<^{CONH_2}_{SO_3OK} + H_2O$.	Found. I.	II.	III.
K	15.21	...	15.18	15.32
H_2O	7.00	7.01	6.88	....

There was no further loss in weight upon heating to 200° C.

Sodium Salt, $C_6H_4<^{CONH_2}_{SO_3ONa} + 2H_2O$. — This salt was made just as the corresponding potassium salt by using sodium hydroxide, and was found to crystallize in transparent prismatic plates from moderately concentrated solutions. Of the crystals,

I. 0.3653 gram lost 0.0509 gram below 150° = 13.95 per cent. H_2O, and gave 0.1002 gram Na_2SO_4 = 8.89 per cent Na.

II. 0.1894 gram lost 0.0263 gram below 150° = 13.88 per cent. H_2O, and gave 0.0533 gram Na_2SO_4 = 9.12 per cent. Na.

	Calculated for $C_6H_4<^{CONH_2}_{SO_3ONa} + 2H_2O$.	Found. I.	II.
Na	8.88	8.89	9.12
$2H_2O$	13.85	13.95	13.88

No further loss in weight occurred on heating to 195° C.

Barium Salt, $\left(C_6H_4<^{CONH_2}_{SO_3O}\right)_2 Ba + 5H_2O$.—This salt was made by boiling the ammonium cyan salt for five hours with a large excess of barium hydroxide. The excess of barium hydroxide was then precipitated with carbon dioxide and the filtered solution evaporated to small bulk. It was found that crystallization did not easily take place even from syrupy solutions, while from dilute alcohol the salt separated in white, arborescent needles arranged in rosettes. Of these crystals,

I. 0.2490 gram gave 0.0928 gram $BaSO_4$ = 21.90 per cent. Ba.

II. 0.3375 gram lost 0.0477 gram below 140° = 14.13 per cent. H_2O, and gave 0.1262 gram $BaSO_4$ = 21.98 per cent. Ba.

III. 0.2169 gram gave 0.0812 gram $BaSO_4$ = 22.01 per cent. Ba.

IV. 0.2596 gram lost 0.0386 gram below 150° = 14.44 per cent. H_2O.

	Calculated for $(C_6H_4{<}^{CONH_2}_{SO_3O})_2Ba+5H_2O$.	Found. I.	II.	III.	IV.
Ba	21.85	21.90	21.98	22.01	....
$5H_2O$	14.35	....	14.13	....	14.44

No further loss in weight took place upon heating to 195° C.

A calcium salt was made in the same manner as the corresponding barium salt, and was found to crystallize in transparent needles. An analysis gave 10.34 per cent. calcium and 19.08 per cent. water lost at 185° C. No formula was found to agree with these results.

A basic lead salt was also made for which no formula could be calculated. It was made by heating the ammonium cyan salt upon the water-bath with a large excess of freshly precipitated lead hydroxide until no more ammonia was given off, and then filtering. Upon cooling there separated crystals composed of white needles, arranged more or less in rosettes. The air-dried salt lost nothing upon heating to 190° and gave the following results:

I. 0.2379 gram gave 0.2068 gram $PbSO_4$ = 59.34 per cent. Pb.

II. 0.1658 gram gave 0.1440 gram $PbSO_4$ = 59.33 per cent. Pb.

III. 0.1860 gram gave 0.1614 gram $PbSO_4$ = 59.29 per cent. Pb.

IV. 0.2735 gram gave 0.1634 gram $PbSO_4$ = 6.31 per cent. S.

V. 0.2772 gram gave 0.1634 gram $PbSO_4$ = 6.22 per cent. S.

Analysis III. was of a second preparation of the salt. The lead was determined by ignition of the salt with addition of sulphuric acid and the sulphur by the Carius method.

Transformation of Orthocyanbenzenesulphonic Acid into Orthosulphobenzoic Acid.

This transformation was effected by heating 2 grams of the ammonium cyan salt with 15 cc. of hydrochloric acid (2 : 1) in a sealed tube for six or seven hours at 190° C. On evaporating to crystallization the characteristic rhomboidal plates of the acid ammonium salt of orthosulphobenzoic acid separated. Of these crystals,

0.4529 gram gave 0.4827 gram $BaSO_4$ = 14.64 per cent. S.

The formula, $C_6H_4<^{COOH}_{SO_2ONH_4}$ requires 14.61 per cent. sulphur.

To further identify this salt it was treated with a slight excess of potassium hydroxide, then acidified with hydrochloric acid and allowed to crystallize. The well-known orthorhombic plates of the acid potassium salt of orthosulphobenzoic acid were obtained, of which,

0.2839 gram gave 0.1032 gram K_2SO_4 = 16.33 per cent. K.

The formula, $C_6H_4<^{COOH}_{SO_2OK}$ requires 16.35 per cent. potassium.

Conclusion.

From this investigation it is clear that orthocyanbenzenesulphonic acid is formed as one of the products of the action of ammonia upon the mixed chlorides of orthosulphobenzoic acid. Moreover, its formation can hardly be explained upon any other hypothesis than that it is derived from a chloride possessing the unsymmetrical formula

$$C_6H_4<^{CCl_3}_{SO_2}>O.$$

It, therefore, appears highly probable that by the action of ammonia an imide is first formed which, being unstable under the existing conditions, passes over by intra-molecular change into orthocyanbenzenesulphonic acid, thus:

$$C_6H_4<^{CCl_3}_{SO_2}>O \rightarrow C_6H_4<^{C:NH}_{SO_2}>O \rightarrow C_6H_4<^{C\equiv N}_{SO_2OH}.$$

JOHNS HOPKINS UNIVERSITY,
NOVEMBER, 1896.

Contribution from the Sheffield Laboratory of Yale University.

XLVI. ON THE NON-EXISTENCE OF TWO ORTHOPHTHALIC ACIDS.

By H. L. Wheeler.

An article on the existence of two orthophthalic acids by W. T. H. Howe, formerly of this laboratory, appeared in the May number of this Journal (page 390). The work described in that article has been repeated, as far as its character would permit, and *it has been found to be impossible to prepare the so-called new or β-phthalic acid by the methods given there.* Every attempt to prepare an acid melting at 184°, *i. e.*, the so-called new or β-acid, from pure materials, resulted only in the formation of the well-known orthophthalic acid melting at or near 203°. Not only has it been found that the methods given by Howe for the preparation of the alleged β-phthalic acid give pure ordinary phthalic acid, but also that his entire experimental work with reference to the new acid, as far as it has been found possible to carry it, is absolutely incorrect.

It will also be shown that the errors are not confined to the experimental work, but that the calculated figures for several analytical results are wrong, and, that in two of these cases, although the analyses of the α- and β-derivatives agree with each other, they do not agree with the correctly calculated figures. Again, statements of Ador and Graebe have not been accurately quoted, and this would lead the reader to incorrect conclusions. Too much stress has been laid on the variation of melting-points of phthalic acid obtained by different observers, since Ador has shown that the melting-points observed by previous investigators were low owing to their having obtained impure samples of the substance. Ador does not state that phthalic acid obtained by "boiling" the anhydride with water melted at 203°, but that by repeated recrystallizations from water such an acid was obtained. Howe further mis-states Ador's work when he says "the acid precipitated from the salts apparently does melt at 180°." What Ador really says is that the *impure* acid precipitated from its salts melts at that temperature. The following is Ador's statement on this subject: "Bei dieser Gelegenheit muss ich die Angaben der Lehrbücher über den Schmelzpunkt der Phtal-

säure (182°) corrigiren. Unreine Phtalsäure schmilzt sogar noch niedriger, bei etwa 170°, durch Ausfällen der Salze dargestellte allerdings bei circa 180°; aus dem reinen Anhydrid durch Wasser gewonnen, mit Thierkohle gereinigt und wiederholt umkrystallisirt, schmelzen ganze Krystalle bei 213°, ihr Pulver bei 203° C."

The next statement to be corrected is that Graebe assumed that 184°, the melting-point given by Lossen, was the correct one for phthalic acid. What Graebe said was that between Lossen's statement and that of Ador, the former was the more correct, *i. e.*, "Lossen's Angabe is die richtigere," since as Graebe goes on to state "Gewöhnlich findet man den Schmelzpunkt etwas höher, bei 190° bis 195°." Graebe then calls attention to the fact that large crystals of phthalic acid, which form according to Ador, melts the highest, could be melted even below 184° if heated for some time.[1] [2]

After giving the above incorrect statements in the introduction to his article, Howe further remarks that "very probably certain low melting-points have been due to an admixture of an acid salt which is precipitated together with

[1] It is well known that the melting-point of orthophthalic acid is really its decomposition-point, *i. e.*, the acid loses water and passes into the anhydride, the melting-point of the anhydride being about 128°. It would be expected that this decomposition might be produced at different temperatures according to the length of time the substance is heated, according to the quantity of substance taken and according to the condition, both physical and chemical, of the sample. Such indeed has been found to be the case. It is therefore not surprising that, if phthalic acid be heated above 128°, different melting-points are obtained under varying conditions.

[2] The author is indebted to Professor Remsen for calling his attention to the following note (This JOURNAL, **3**, 30.) on the melting point of phthalic acid, which was not known to the author when the above was written. "The fusing point of phthalic acid has been the subject of considerable discussion, the last statement bearing upon it having come from E. Ador (Annalen der Chemie, **164**, 239). Ador says tha crystallized phthalic acid melts at 213° and the powder of the same substance at 203° The discrepancies in the statements on record seems to be due to the fact that when the acid is heated, it is partly converted into its anhydride before its fusing point is reached. The presence of the anhydride tends to lower the fusing point, and this is the lower the more anhydride there is formed. If the acid is heated slowly, or if it be used in the form of powder more anhydride is formed and the fusing point is lower. Some special experiments were made with the pure acid to test the correctness of this view. Small quantities were heated in U-tubes placed in paraffin baths at the temperature of 140° and 170°. In both cases anhydride was formed and the fusing point of the acid considerably lowered. Under exceptional conditions the fusing point of pure phthalic acid may be observed as high as 213°, but usually it will be found to vary considerably. To test the purity of the acid, it is advisable to make the anhydride and then crystallize this, when pure, from water.—I. R."

the acid under certain conditions of concentration," and on page 394 he again states that by acidifying concentrated alkaline solutions of phthalic acid a white crystalline precipitate is thrown down. "This is identical in appearance with the pure acid, but it melts at 175°–180°, and upon drying and extracting with alcohol a residue of an acid salt remains." This is also incorrect, because the writer has prepared the acid salt of phthalic acid and mixed it with varying proportions of the acid without observing that it produced such an effect on its melting-point. The acid salt itself did not melt below 270°. [Compare also Eighth Experiment below.]

EXPERIMENTAL WORK.

Attempts to Prepare the β-Acid by the First Method.

Howe states that "to prepare the pure β-acid, the anhydride is dissolved in cold dilute sodium hydroxide, the solution cooled to 0°, slowly precipitated with hydrochloric acid and dried over sulphuric acid." The attempts to prepare the β-acid according to these directions were conducted as follows :

First Experiment.—Finely powdered phthalic acid anhydride[1] was dissolved in cold, very dilute sodium hydrate and filtered. During these operations the temperature of the solutions did not rise above + 5°. It was then cooled in a freezing-mixture to — 3°, and cold dilute hydrochloric acid was slowly and cautiously added in excess. During the neutralization the temperature of the solution did not rise above + 1°. The solution was so dilute that after an excess of hydrochloric acid was added, no immediate precipitate separated, but, on standing, a well crystallized product was obtained in small amount. This was filtered, washed with ice-water and prepared for a melting-point determination by drying, in the air, and then pulverizing the material. This specimen, according to Howe, should melt at 184°, but, when the heating was started at an ordinary temperature, it showed absolutely

[1] Phthalic acid anhydride, manufactured by H. Trommsdorff, of Erfurt, Germany, was used in these experiments.

no signs of melting below 193°, finally melting with effervescence at 200°.[1]

Another portion of the same material was taken, and the heating was started at 180°; it then melted at 203° and showed no signs of melting below 197°.

Another portion dried over sulphuric acid gave a melting-point of 206° when the heating was started at 197°. Finally, another portion of this material was placed in the melting-point apparatus at 75°, heated rapidly up to 128°, and then half an hour was taken to heat the material up to 184°; even then no trace of melting could be observed below 190°, when it slowly began to melt, and at 193°.5 effervescence took place.

These melting-points show that nothing but ordinary phthalic acid was obtained in this experiment, and that the melting-point of the acid varies according to the length of time employed in heating.

Second Experiment.—Finely powdered phthalic acid anhydride (4.0 grams) was dissolved in a five per cent. solution of sodium hydrate (4.0 grams of sodium hydrate) at + 6°. The solution was cooled to — 4° and slowly precipitated by adding a 20 per cent. solution of hydrochloric acid *drop by drop*. The neutralization was conducted at temperatures ranging from — 4° to + 1°. The solution was made strongly acid and then allowed to warm up to + 6°. It was filtered, washed with ice-water, and one portion dried in the air, the other over sulphuric acid. The portion dried in the air melted at 201°, while that dried over sulphuric acid, the melting-point being determined by a different observer, melted at 200°. There-

[1] The melting-points given in this paper were taken in the usual manner unless otherwise stated. The contents of the melting-point flask were 78.5 cc. and in this flask 37 cc. of concentrated sulphuric acid were placed. The thermometer was made of normal glass. It was obtained from Drs. Bender and Hobein, of Munich, and it was graduated in degrees ranging from — 29° to 360°, the 200° mark was 1.4 of a degree too low according to a "Prüfungs-Bescheinigung," which accompanied the thermometer. The thermometer was further tested by taking a melting-point of paranitroacetanilide. This substance was prepared from the base and crystallized from strong alcohol. The second and third crystallizations began to show signs of melting at 207°.5, and then melted together at 208°.5, as near as could be judged. The generally accepted melting-point of paranitroacetanilide is 207°. This result therefore confirms the statement in the "Prüfungs-Bescheinigung." *The correction has not been applied to the melting-points given in this article.*

fore in this experiment also nothing but ordinary phthalic acid was obtained.

Third Experiment.—In this experiment 20 grams of anhydride were dissolved in 30 grams of sodium hydrate in 170cc. of water, and the solution was precipitated with 20 per cent. hydrochloric acid without carefully cooling. The product thus obtained was dried in the air and portions placed in two capillary tubes, one of which had a diameter of 1.0 mm., while the other was oval-shaped and measured 3.0 mm. by 2.0 mm. The portion in the smaller tube melted at 193°, while that in the larger tube melted at 197°, although they were side by side in the melting-point apparatus.

Again portions of the same material were placed in two tubes as follows: One tube was 1 mm. in diameter, the other 3.0 mm. by 4.0 mm. These tubes were placed side by side and the melting-points determined as 198°, at which temperature the substance in the smaller tube melted with effervescence. The heating was then discontinued, and not until the effervescence in the one tube had almost ceased, did the other begin.

This experiment shows that nothing but ordinary phthalic acid was obtained, and that the melting-point of this acid depends not alone on the time taken in heating, but that it also may vary with the amount of substance used.

Fourth Experiment.—In this experiment a much stronger solution of sodium hydrate was used to dissolve the anhydride than that used in the previous cases. The solution cooled to 0° was then very slowly precipitated with hydrochloric acid. A product was thus obtained, which, when dried over sulphuric acid, melted in powdered form at 204°, the crystals at 205°. This material was therefore the ordinary acid, and since no evidence was found that the anhydride gave anything else when treated according to Howe's directions, further attempts to prepare the so-called β-acid by this method were abandoned.

Attempts to Prepare the β-Acid by the Second Method.

Howe's second method for preparing the "new acid" is as

follows: "The α-acid is converted into the β-isomer by boiling with a 30 per cent. sodium or potassium hydroxide solution for four or five hours, then precipitating and drying as mentioned above."

Fifth Experiment.[1]—35 grams of the ordinary or "α-acid," which had been obtained by the previous attempts to prepare the "β-acid" were boiled with a 30 per cent. solution of sodium hydroxide, the calculated quantity of sodium hydroxide to convert the acid into its sodium salt being previously added. The boiling was continued without interruption for five hours and a half. A portion of the solution, which on cooling became semi-solid, was then taken, diluted with 3 to 4 volumes of water and cooled in a freezing-mixture of ice and concentrated hydrochloric acid. The solution was then neutralized with 20 per cent. hydrochloric acid, so carefully that the temperature did not rise to 0° during the entire operation. A well crystallized product separated soon after an excess of acid was added. This was filtered, washed with ice-water and dried by pressing on paper and exposure to the air at ordinary temperature. It then melted sharply from 203°-4°, and was therefore pure ordinary phthalic acid.

Further attempts to prepare the compounds melting at 184° and described as β-phthalic acid from pure phthalic acid or its anhydride were deemed useless, and experiments along these lines were therefore abandoned. It seemed of interest, however, to see if pure phthalic acid was affected by strong acids, since Howe states that "strong acids partially change the α- into the β-acid."

Sixth Experiment.—A portion of the pure phthalic acid, melting at 203°, from the fifth experiment was digested with concentrated hydrochloric acid for an hour at ordinary temperature; water was then added without trying to avoid the rise in temperature that was produced. The product when dried showed absolutely no appreciable change in the melting-point.

Seventh Experiment.—In this experiment the pure phthalic acid was dissolved in a large excess of concentrated sulphuric

[1] In the performance of this experiment the author was assisted by Prof. H. L. Wells, to whom he wishes to express his thanks.

acid at ordinary temperature, in which it is readily soluble; water was then poured into the acid, when the solution of course boiled, and, on cooling, a well crystallized product was obtained, and, when dried, melted unaltered at 203° to 205°. Strong acids therefore do not "partially" change ordinary pure phthalic acid into a "β-acid."

Eighth Experiment.—A portion of the semi-solid mass from the fifth experiment, which consisted of the sodium salt of phthalic acid, suspended in a strong solution of sodium hydrate, and in which it is difficultly soluble, was treated directly with strong hydrochloric acid; this brought about solution and then gave a precipitate of the acid salt as stated, but the precipitate thus produced remained unaltered even at the boiling-point of sulphuric acid, while it is stated by Howe that this precipitate melts from 175° to 180°.

The Analytical Results.

Howe's results obtained with the aniline salts are remarkable, as both agree with an error in calculation for carbon that is almost two per cent. too low. They are as follows:

	Calculated for $C_{20}H_{16}N_2O_4$.		Found.	
	Correct.	Incorrect.	α-Salt.	β-Salt.
C	68.18	66.30	65.92	66.01
H	5.68	5.53	5.72	5.63

In the case of the brucine salts the error is even greater. Here the analyses of the two products agree only with each other, and the determinations found are over four per cent. too high.

	Calculated for $C_{54}H_{58}N_4O_{12}$.		Found.	
	Correct.	Incorrect.	α-Acid (?).	β-Acid (?).
C	67.92	78.81	72 22	72.35
H	6.07	6.52	6.82	6.89

Since there is so great a variation in the case of the carbon between the theory as given and the analyses as reported, it is possible that a typographical error has occurred and each of the figures 8 should be read as a 2. This seems possible, since a typographical error in the references occurs on the first page of the article, where a figure 2 has been printed as a 9. The reference in question is number 3, and instead of Ber.

d. chem. Ges., **19**, 579, should read Ber. d. chem Ges., **12**, 579.

The error in the case of the α-naphthylamine salts is about one per cent. for carbon, and seems again to be typographical since both preparations agree with the correct theory.

	Calculated for $C_{32}H_{24}N_2O_4$.		Found.	
	Correct.	Incorrect.	α-Salt.	β-Salt.
C	74.34	73.34	74.22	74.15
H	5.31	5.21	5.42	5.51

Conclusion.

Since it has been shown in this article that the β-phthalic acid does not exist, or rather cannot possibly be prepared from pure materials by the methods given by Howe in his article, it follows that the number of derivatives described by him also can not be prepared by his methods, and it is naturally impossible to repeat the rest of his experimental work on the derivatives of the alleged new acid. If one removes the foundation of a piece of work, naturally the whole structure falls to the ground. It may be said in conclusion that the results of the present investigation show that the methods given by Howe, when carefully followed, do not give any clue whatever to the real nature of the compounds which he prepared. The work described in this article was undertaken at the request of Prof. H. L. Wells.

NEW HAVEN, OCTOBER, 1896.

Contributions from the Laboratory of Analytical Chemistry of the University of Michigan.

A PURE CARBIDE OF IRON.

BY E. D. CAMPBELL.

The first definite carbide of iron described was that obtained by Sir F. Abel and Mr. Deering,[1] who isolated it by acting upon thin sheets of annealed steel with a mixture of dilute sulphuric acid and potassium dichromate. The results of analyses of residues thus obtained, while not agreeing very closely, led the authors to assign the formula Fe_3C to the carbide existing in annealed steel. Later Dr. Müller,[2] by the action of dilute sulphuric acid upon annealed steel recov-

[1] Proceedings Inst. Mech. Eng., 1885, p. 30.
[2] Stahl und Eisen, No. 5.

ered about one-half of the carbon in the steel in the form of a carbide, also agreeing approximately with the formula Fe_3C. Osmond and Werth,[1] by acting upon steel electrolytically in dilute hydrochloric acid solution, according to the method first proposed by Weyl, obtained a dark residue containing thin metallic plates, which they proved both microscopically and chemically to be identical with the carbide first isolated by Abel. The latest and most exhaustive work that has appeared was that by J. O. Arnold and A. A. Read.[2] These authors prepared five samples of steel of varying carbon content, and, after carefully annealing them, submitted them to electrolytic action in hydrochloric acid solution for varying lengths of time. The carbonaceous residue adhering to the bars was scraped off, and, after washing till free from ferrous chloride, was rinsed into a porcelain boat and subsequently burned in a stream of oxygen for the determination of carbon, the iron being determined in the residual ferric oxide. In this way the weight of steel dissolved in the different experiments varied from 3.466 grams to 10.238 grams, yielding residues weighing from 0.0697 gram to 0.8912 gram. The percentage of carbon in the residues obtained varied from 6.60 to 7.83 per cent., 6 out of 8 determinations lying between 6.60 and 6.97 per cent., the theoretical percentage of carbon for the compound Fe_3C being 6.67 with 93.33 per cent. of iron. These residues were described as varying in color from "dull grey, silver plates mixed with greyish-black powder" to "silver grey plates." The proportion of carbon in the residues varied from 71.31 to 94.90 per cent. of the total amount in the steel.

The following research was undertaken to determine if a purer carbide than any heretofore isolated could not be obtained, and whether a formula so simple as CFe_3 should be assigned to it. The steel used in the work was a sample of crucible cast steel containing 1.29 per cent. of carbon. This steel was rolled into bars 5 cm. wide and 1.5 cm. thick, then cut into lengths of 30 cm. These pieces were annealed in the following manner: The bottom of an ordinary assay muffle

[1] Annales des Mines, 1885, Vol. 2.
[2] J. Chem. Soc., 1894, **65**, 788.

furnace was covered to the depth of 6 or 8 mm. with crushed coke. Upon this was placed sheet asbestos, then the bars were introduced. On top of the bars sheet asbestos was also placed, and the rest of the space in the muffle completely filled with a mixture of one part charcoal to five of wood ashes. The whole of the space in the front of the muffle was filled with this mixture and the door closed. The muffle was then brought to a bright red heat, the fires banked, and the whole allowed to cool slowly. At the end of sixty hours the bars were still warm.

The bars, after annealing, were freed from scale by grinding on an emery wheel, and were then cut into strips from 5 to 6 mm. in thickness. These strips were then cut in two, giving for the final pieces used in the work small bars about 15 cm. long, 15 mm. wide, and from 5 to 6 mm thick.

The electrolysis of the bars was carried on in a manner quite similar to that used by Arnold and Read, but with such modifications of the apparatus as were thought suited to the larger samples used in the work. Each bar was sawed near one end about half way through, thus practically making a small hook, by means of which the bar could be easily hung to a small platinum wire stirrup soldered to a copper wire hook about 10 cm. long. Twelve of these hooks with their attached bars were hung to a ring of heavy copper wire about 10 cm. in diameter, which was fastened to a large retort stand, and connected with the positive pole of 4 storage batteries, connected in series, and having an electromotive force of about 8 volts. The negative pole consisted of a small platinum cylinder suspended in a porous cup standing in the centre of the circle of bars.

An ammeter and resistance box were introduced into the circuit so that the current passing through the bars could at any time be easily read and controlled. The bars and porous cup, during the electrolysis, were nearly immersed in 4 per cent. hydrochloric acid (1 volume of hydrochloric acid, sp. gr. 1.20, to 12 of water) contained in a large beaker, about 2 liters being used each time.

The method of operating found most satisfactory was as follows: When the bars were hung in position a current of 1

ampere was started through the system, and allowed to act over night, usually about fifteen or sixteen hours. A small brown deposit, varying in amount, was noticed accumulating around the negative pole and, according to whether this was present in large or small amounts, the current would be found to have fallen to from 0.6 to 0.9 amperes. In the morning the bars were all removed from the acid and placed in a large dish of water. They were then taken and the residue adhering to the surface of the bars brushed off by rubbing with a small brush made by binding together a large number of strands of fine No. 28 pure aluminium wire. After the bars were brushed clean they were placed under water and allowed to remain until afternoon, when the system was again set up, fresh acid being used each day. An aluminium wire brush was used, as earlier work showed that a brush made of rubber or bristles was quickly cut by the sharp crystals, and the residue contaminated with organic material. The small pieces of aluminium, which were broken off by the vigorous rubbing necessary to remove the carbide, were easily removed by dissolving in potassium hydroxide.

When the carbide had been brushed from all of the bars it was collected in a small beaker, washed well by decantation with distilled water, then treated with warm 10 per cent. potassium hydroxide until all particles of aluminium were dissolved. The potassium hydroxide was then decanted, and the carbide again well washed with distilled water by decantation. During these latter decantations the material was thoroughly stirred, and the solution decanted before any very fine or light matter had time to settle. This was done until only a heavy, bright steel-gray powder remained in the beaker. This carbide was then thrown on a smooth lintless filter, washed with alcohol, then with ether, dried, weighed, and placed in bottles for further investigation.

The original weight of the twelve bars operated upon was 1352.3 grams. At the end of 29 electrolyses the weight was 776.5 grams, showing 575.8 grams of steel to have been dissolved. The actual weight of carbide recovered, not including what must have been lost in washing by decantation, to remove uncombined carbon, was 55.1 grams, or 9.66 per cent.

of the steel dissolved. Had all of the carbon in the steel been recovered as the carbide CFe_4, there would have been 19.35 per cent. of carbide. Thus the amount actually recovered was one-half that present in the steel. Part of the loss was undoubtedly due to a mechanical action in washing the carbide to insure perfect freedom from uncombined carbon, although probably the greater part of the loss was due to compounds dissolved by hydrochloric acid.

The carbide obtained by the above process consisted of a bright steel-gray powder, which, on examination with a microscope, was found to be made up of thin plates or scales. The specific gravity determined on a sample of about 15 grams at 23° was 6.944. The carbon was determined in two samples of 5 grams each recovered at different times, the method used being that of decomposition with slightly acid potassium cupric chloride, and subsequent combustion of the carbon in oxygen. The iron was determined gravimetrically as ferric oxide and checked volumetrically. The carbide showed the following composition:

	Per cent.
Carbon	6.646 and 6.625
Iron	93.255
Phosphorus	0.026
Manganese	none

This carbide is gradually, but completely, converted into ferric oxide and carbon by oxidation in moist air.

5.0263 grams, placed in a watch-glass, was alternately moistened with distilled water and dried in an air-bath at about 80° C. once or twice each day until the weight became constant.

This required about six weeks. The result was a brownish-red powder weighing 7.066 grams, thus showing a gain in weight by oxidation of 2.040 grams. This oxidized product, on treatment with hydrochloric acid, left an insoluble black residue which, on combustion, gave 4.64 per cent. of carbon, equal to 6.64 per cent. of the original carbide. The theoretical amount of oxygen necessary to convert the iron in 5.0263 grams of carbide to Fe_2O_3 is 2.009 grams, whereas the gain in weight was 2.040 grams. The slight excess is probably due

to water combined with the carbon, the ferric oxide being anhydrous.

The carbide was, practically, completely soluble in hot moderately concentrated hydrochloric acid, so that it was thought desirable to study the products of solution, as they would probably throw some light on the constitution of the body from which they were derived.

The gaseous products of solution were obtained in the following manner: A small generating flask, having a capacity of about 150 cc., was fitted with a 3-hole rubber stopper. Through one hole passed a tube connected with a carbon dioxide generator, rendering it possible to displace all of the air in the flask by carbon dioxide. Through a second hole passed a long funnel, provided with a stop-cock, and drawn out at its lower end to a fine opening. Through the third hole passed the outlet tube, which was surrounded by a short reflux condenser, and was fused to a 3-way stop-cock. One arm from the 3-way stop-cock opened into the air, the other was connected with one tip of a specially constructed Hempel gas burette, graduated to 200 cc. and accurately calibrated. The second tip of the Hempel burette was connected by means of capillary tubing to a Hempel storage pipette filled with mercury, but containing 3 or 4 cc. of 1 to 1 potassium hydroxide. The burette was water-jacketed and filled with mercury.

In collecting the gas, the sample of 0.600 gram of carbide was first introduced into the generating flask and covered with a small amount of water. The level-bulb of the collecting burette was then lowered until the solution of potassium hydroxide in the storage pipette was drawn over to the stop-cock of the burette, which was then reversed and the air in the burette completely expelled by raising the level-bulb until the mercury completely filled the burette and just reached the three-way stop-cock between the generating flask and the burette. In this way the entire space beyond the 3-way stop-cock was filled with mercury. The 3-way stop-cock was then turned so as to connect the generating flask with the outside air, and carbon dioxide run into the flask until complete absorption by potassium hydroxide showed all of the air in the

flask to have been displaced. The supply of carbon dioxide was then shut off, and the 3-way stop-cock turned so as to connect the generating flask with the collecting burette. The stop-cock of the funnel which had been previously filled with 1 to 1 hydrochloric acid was then opened, and a little hydrochloric acid allowed to run into the flask, which was then heated until action set in. As soon as gas began to be evolved, the stop-cock of the collecting burette was opened so that the gases might pass over, the mercury in the level-bulb being kept level with that inside of the burette, thus avoiding any excessive internal pressure. When the collecting burette was nearly filled with gas the stop-cock of the burette was reversed, and this gas driven over into the storage pipette, and then the stop-cock brought back again to its original position, and the collection continued.

Solution could be easily completed in about an hour by gradually increasing the amount of hydrochloric acid added, and bringing the contents of the flask to active ebullition. When solution was complete the 3-way stop-cock was closed, the funnel filled with hot water, and the flame withdrawn from under the flask. As the steam condensed, the flask drew in sufficient water to nearly fill it. The 3-way stop-cock was then opened to once more connect with the collecting burette, the mercury in the level-bulb lowered, until all of the gas in the generating flask had been drawn over to the burette, water being allowed to run in through the funnel during the operation. When the last of the gas had been transferred to the collecting burette, its stop-cock was reversed, and all of the gas passed over into the storage pipette, and allowed to stand until the carbon dioxide was completely absorbed. When the carbon dioxide was all removed, the gas was passed back from the storage pipette into the collecting burette, and its volume read, and corrections made for temperature, pressure, and vapor-tension, the volume being reduced to standard conditions, dry gas at 0° C. and 760 mm. pressure. In this way about 150 cc. of gas were obtained from each solution.

This gas was analyzed first for the total carbon dioxide obtained by combustion of both paraffins and olefins. This

combustion was effected in the usual manner by mixing 12–14 cc. of the gas with enough air to make 100 cc. exploding in an explosion pipette, and determining the carbon dioxide by absorption with potassium hydroxide.

The volume of the olefins was determined by operating directly in the 200 cc. collecting burette. After sufficient gas had been drawn off in a second burette for the determination of total carbon dioxide from paraffins and olefins, the gas remaining in the collecting burette was measured; then by means of a small funnel attached to one tip of the burette, about 2 cc. of 1 to 1 potassium hydroxide was introduced into the burette.

When the mercury was so protected, a few small drops of bromine were allowed slowly to run into the burette, thus filling it with vapor of bromine, which soon formed the dibrom derivatives with the olefins. When all of the bromine had been absorbed the entire volume of gas, together with the solution of potassium hydroxide in the burette, was passed into the storage pipette, and sufficient mercury to fill the connecting capillary was forced over; then the storage pipette was pinched off. The mercury in the collecting burette was now emptied, and the burette and mercury thoroughly washed with water, then with dilute sulphuric acid to neutralize any potassium hydroxide, and finally with water again. The mercury was then replaced, the burette connected with the storage pipette once more, and the gas returned and measured, the loss in volume giving the volume of the olefins.

The residual gas contained hydrogen and the paraffins. A sample of this gas was transferred to a second burette, mixed with air, and exploded for the determination of the carbon dioxide derived from the paraffins. The volume of carbon dioxide derived from the olefins was taken as the difference between the results obtained in the first and second explosions.

Owing to the fact that the paraffins are higher members than methane, the volume of hydrogen could not be determined by the contraction in the explosions, so that the method proposed by the author,[1] that is, direct absorption of the hydrogen with 1 per cent. palladious chloride was re-

[1] This JOURNAL, 18, 294.

sorted to. Samples of the gas, from which the olefins had been removed, were passed into absorption pipettes filled with palladious chloride, and heated until absorption of the hydrogen was complete. As soon as the absorption of hydrogen in one sample was about complete the residual gas was returned to the burette and a second sample of gas drawn in and mixed with it. The combined gases were then returned to a pipette filled with fresh palladious chloride, and the absorption continued. This method of removal of hydrogen and accumulation of paraffins was continued until sufficient of the paraffins was obtained for satisfactory explosions.

Owing to the fact that dilute mixtures of the paraffins with air do not readily explode on sparking, a small measured amount of pure hydrogen was introduced, each time allowance being made, of course, for this contraction. The paraffins obtained by this method gave an explosion for every volume of gas burned, almost exactly two volumes of carbon dioxide, accompanied by a contraction of 2.5 times the gas burned, and an oxygen consumption of almost exactly 3.5 volumes, thus indicating that ethane C_2H_6 was probably the paraffin present.

The volume of hydrogen was obtained by taking a sample of the gas from which the olefins had been removed, mixed with an accurately measured amount of nitrogen, and passing into palladious chloride, keeping the gas over palladious chloride for periods of time varying from two to fourteen hours. A measured amount of nitrogen was introduced, since the volume of paraffins, after the removal of the hydrogen, would be so small as to render the reading inconvenient if not impossible.

In the following table the amount of gases which was obtained from one gram of the carbide is given :

Gas evolved.	Hydrogen in cc.	Total CO_2.	CO_2 from paraffins.	CO_2 from olefins.	Volume of olefins.
250.51	208.10	71.87	35.68	36.20	
250.51	208.10		34.80	37.00	
250.77		75.09	30.10	45.09	9.32
251.80		71.05			9.47
250.77			31.89	43.20	9.93
251.90	213.10	70.80	30.40	40.40	9.88
251.90	213.10	71.87	35.68	36.20	

The above "total CO_2" would contain only enough carbon to account for about 60 per cent. of the carbon in the carbide dissolved, thus showing that nearly 40 per cent. was present in the form of some hydrocarbon, which was either condensed or remained in solution in the generating flask. The strong odor, both of the solution in the generating flask and especially of the potassium hydroxide used in the storage pipette for the removal of the carbon dioxide, showed that butane was undoubtedly present, and it is probable that the greater part of the carbon unaccounted for was lost in this form. The most striking feature in the above table is the volume of carbon dioxide derived from the olefins compared with the volume of the olefins. It will be noted that this ratio is a little more than 4 to 1, thus indicating the almost certain predominance of butylene, C_4H_8, probably mixed with a little dibutylene, C_8H_{14}.

As early as 1864 Hahn,[1] and again in 1877, Cloëz[2] showed, by dissolving cast irons in dilute hydrochloric or sulphuric acid, that a portion of the carbon passed off with the hydrogen as ethylene, C_2H_4, propylene, C_3H_6, butylene, C_4H_8, and dibutylene, C_8H_{14}. This they showed by passing the gas through bromine and purifying and fractionally distilling the dibrom derivatives thus obtained.

At the time of Hahn's and Cloëz's work no definite carbide of iron had been isolated, and no possible explanation offered for the presence of the gaseous products of solution of a mixture of hydrogen, olefins and paraffins. We would recall two well-known facts before offering a possible explanation for the composition of the gas evolved in dissolving iron containing carbon. The first of these is the tendency of the olefins with the general formula, C_nH_{2n}, to combine with nascent hydrogen to form the corresponding paraffins, C_nN_{2n+2}; and also the tendency of some of the higher olefins, especially butylene, C_4H_8, and those of higher molecular weight to form condensation products. It would seem not unreasonable to assume that iron is capable of forming a series of what we might properly term ferro-carbons analogous to the olefin series of hydrocarbons; that this series has the general formula,

[1] Ann. Chem. (Liebig), **129**, 57. [2] Compt. rend., **85**, 1003.

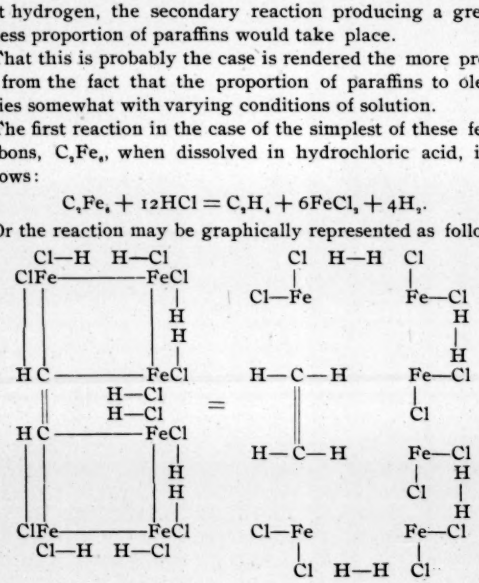
C_nFe_{2n}, in which the group $\begin{matrix}Fe—Fe\\ |\quad\ |\\ \quad —Fe\end{matrix}$ replaces H_2 in the olefin series C_nH_{2n}; that, when these ferro-carbons are acted upon by an acid, such as hydrochloric or sulphuric acid, the first reaction is the substitution of two hydrogen atoms for the two iron atoms, united to the carbon atom, thus producing the analogous olefin, C_nH_{2n}, free hydrogen being liberated between the iron atoms. Thus the primary products of solution of these ferro-carbons would be olefins, C_nH_{2n}, and hydrogen, but, owing to the tendency of the olefins to combine with nascent hydrogen, the secondary reaction producing a greater or less proportion of paraffins would take place.

That this is probably the case is rendered the more probable from the fact that the proportion of paraffins to olefins varies somewhat with varying conditions of solution.

The first reaction in the case of the simplest of these ferro-carbons, C_3Fe_4, when dissolved in hydrochloric acid, is as follows:

$$C_3Fe_4 + 12HCl = C_3H_4 + 6FeCl_2 + 4H_2.$$

Or the reaction may be graphically represented as follows:



The secondary reaction between hydrogen and the olefins would be one of direct addition to form the homologous paraffins.

Further work upon the relation of iron to carbon in continuation of what has been carried on in this laboratory during the past four years, will be prosecuted in the hope of giving greater weight to the above hypothesis, and of determining if possible the conditions governing the formation of the various ferro-carbons, and the influence of their compounds upon the physical properties of the iron or steel in which they occur.

I wish here to express my obligations to my two assistants, Messrs. Walter Scotten and Firman Thompson, for the care with which they carried on the laboratory work in the recovery and analysis of the above carbide.

ANN ARBOR, MICHIGAN.
OCTOBER 23, 1896.

THE ALKALI TRIHALIDES.

BY CHARLES H. HERTY AND HOMER V. BLACK.

It has been shown by one of us[1] that the so-called compounds PbICl, $PbI_2.2PbCl_2$, $PbI_2.5PbCl_2$, described by Labouré,[2] Poggiale,[3] and Miss Field,[4] are not true chemical compounds, but isomorphous mixtures of lead iodide and lead chloride. This suggested the thought that possibly the mixed trihalides of the alkali metals were also isomorphous mixtures and not true chemical compounds.

To determine this point it was deemed best to study one of the series of rubidium trihalides described by Wells.[5]

Messrs. Eimer and Amend have kindly furnished us with a quantity of rubidium iodide sufficient for the investigation.

The method of work consisted in determining the composition of the successive crops of crystals obtained from a solution of the ingredients in quantities suitable for giving as the first crop the member of the series under investigation.

Our work has been confined to rubidium dibromiodide. To prepare this substance 10 grams of rubidium iodide were dissolved in 6.6 cc. of water. To this solution was added very cautiously 8 grams of bromine. At first separation of iodine occurred. On stirring, this completely dissolved, the solution

[1] This JOURNAL, **18**, 293.
[2] J. Pharm. [3], **4**, 328.
[3] Compt. Rend., **20**, 1180.
[4] J. Chem. Soc., **63**, 540.
[5] Am. J. Sci., **43**, 475.

becoming warm. On cooling and standing for several hours, quite a large crop of crystals was obtained. These crystals resembled in every way those obtained by Wells. They were quickly dried between folds of paper and immediately placed in a desiccator. They were designated "A."

The mother-liquor from "A" was allowed to evaporate spontaneously, and thus a second crop of crystals was obtained, similar to "A." These were designated "B."

Further evaporation of the mother-liquor from "B" gave a third crop of crystals, similar to "A" and "B." These were slightly mixed with crystals of a normal halide, from which they were carefully separated. The third crop was designated "C."

In these substances rubidium was determined by heating the substance in a porcelain crucible. Only rubidium bromide remained in each case after the heating. Bromine and iodine were determined by treating the water solution of the substance with sulphurous acid, just sufficient for decolorization, precipitating the halides with excess of a standard solution of silver nitrate, weighing the precipitated silver halides, and determining the excess of silver in the filtrate by ammonium thiocyanate. The results of the analysis are given below:

	A.	B.	C.	Calculated for $RbBr_3I$.
Rb	22.99	22.92	22.88	22.95
Br	39.64	41.23	40.41	42.97
I	37.07	35.94	36.66	34.08
Total	99.70	100.09	99.95	100.00

From these results it is evident that the three successive crops of crystals are identical, proof being thus given that the substance is not a mixture, but a true chemical compound.

When this salt is dissolved in water, dissociation takes place as is shown by the odor of the solution. Complete dissociation, however, does not take place immediately, for when silver nitrate is added to the dilute water solution of the substance, the precipitate is at first quite dark. This gradually changes to the lighter color of silver bromide and silver iodide. Not enough of this dark precipitate was obtained in satisfac-

tory condition for analysis, but it seems probable that the substance has the composition $AgBr_3I$.

The stability of the salt $RbBr_3I$ is quite marked in the absence of moisture.

1.4047 grams $RbBr_3I$ on standing in a desiccator 16 days lost only 3.3 milligrams. On standing 38 days the loss was only 7.1 milligrams.

The effect of atmospheric moisture in accelerating the decomposition of this salt is well shown in the following table:

Time of standing.	Condition of experiment.	Per cent moisture in air.	Weight of salt. Gram.
	Original weight of salt		0.8678
2 days.	In open vessel		0.8655
1 day more.	" desiccator		0.8650
1 " "	" "		0.8649
1 " "	" open vessel		0.8644
1 " "	" " "	69 per cent.	0.8642
1 " "	" " "	69 " "	0.8640
2 days "	" " "	92 " "	0.8632
2 " "	" " "	93 " "	0.8627
4 hours "	" desiccator		0.8626
20 " "	" "		0.8625
5 days "	" "		0.8622
21 " "	" "		0.8582

The addition of a slight quantity of sulphurous acid to the water solution of the salt produces a precipitation of iodine, which is redissolved on further addition of the reagent.

Finally to 10 grams of rubidium iodide dissolved in 6.6 cc. of water was added 4 grams of bromine, one-half of the quantity of bromine used in the preparation of rubidium dibromiodide. From the solution thus obtained only rubidium triiodide crystallized as the first crop.

UNIVERSITY OF GEORGIA,
JUNE 27, 1896.

ACTION OF WATER OF THE HUBB COAL MINE UPON CAST IRON.

BY FRANK W. DURKEE.

In 1872 the Hubb Coal Mine, in Cape Breton, Nova Scotia, was abandoned. Soon it filled with water; but in the time between December, 1894, and April, 1895, the Dominion Coal

Company (Limited), the present owners of the mine, pumped the water out. Then, it was found, that the cast iron which had formerly been used for purposes of construction within the mine, had, while lying beneath the mine water, through this long period, undergone radical changes. For instance, the cast iron T-rails in the car tracks, while retaining their original size and shape, were no longer strong and fairly tough like cast iron. A man could break them across his knee, or beat them into fragments with a tack hammer. They were soft enough to be easily cut with a knife. A cross-section, prepared by the use of an ordinary saw, was grayish-brown in color. The internal half of the section, however, was lighter in color than the external, and softer in texture. Where the surfaces of the original castings were not covered by films of a reddish-brown ferric oxide, they were grayish-brown like the cross-sections. The transformed cast iron was magnetic, porous, and several times lighter than the same bulk of cast iron. Brought in contact with a piece of white paper it left a mark like that of a lead pencil. In a word, the greater part of the cast iron that was in the Hubb mine at the time it was filled with water, had been changed, by chemical action, into masses looking like graphite and shaped like the original castings. While the changes described above had been going on in the cast iron, the surfaces of wrought iron structures had been deeply corroded by the mine waters, but the iron in the deep-seated portions still remained perfect. Consequently the wrought iron structures in the mine had diminished considerably in size, but internally had not become porous like the cast iron. Steel structures had wasted away but slightly, and were perfect beneath their surfaces. The waters of the Hubb mine attack white cast iron less readily than gray, wrought iron slowly, and steel with much difficulty.

Changes in cast iron, in some ways, not unlike those that have taken place in the Hubb mine, have been described by Deslongchamps,[1] who found that the cast iron cannon balls, which had been taken from the sea off the coast of Normandy, had lost two-thirds of their weight, contained no metallic

[1] J. chim. Méd., 13, 89.

iron, and were soft enough to be cut with a knife. Berzelius states[1] that some of the cast iron cannon balls, which had been taken from a vessel, sunk fifty years before near Carlscrona, were changed to their very centers into a gray, porous, graphite substance, which, after exposure to the air for fifteen minutes, became hot enough to drive out the adhering moisture. Other cannon balls in the same lot were changed, as above described, only through a part of their diameters. In the opinion of Berzelius and Karsten, these changes have been produced by the action of oxygen and carbon dioxide from the atmosphere, which have been dissolved in the sea water, and they describe the product as a mixture of graphite, ferric oxide, ferrous carbonate, silica, and the carbide of iron, FeC_3. Karsten has also shown that a mixture of graphite, silicon, and the carbide, FeC_2, is produced by treating gray cast iron with a ten per cent. solution of sulphuric acid. Mallet has found[2] that cast iron yielded more readily to the action of impure waters at the mouths of rivers which empty into the sea, than to the action of pure sea water. The chemical changes that take place under the last mentioned conditions, Mallet summarized as follows: $FeO + H_2O$, $Fe_2O_3 + FeO + H_2O$, and $FeCO_3$, are at first produced. These substances are then attacked by H_2S, forming FeS and $6(FeS + FeS_2)$. The sulphides are transformed by the oxygen of the air into $2Fe_2O_3 + SO_3 + 6H_2O$ and $FeSO_4 + 6H_2O$.

It is noticeable, in all the instances hitherto investigated, where cast iron has been transformed by natural means into the product above described, that the transformation has been effected under sea water, or in a mixture of sea water and fresh water, where the conditions are different from those that might be expected to exist in a submerged Nova Scotia coal mine. Consequently, to find by what means the cast iron of the Hubb mine had been changed to a mass resembling graphite, and the chemical character of the new substance, further investigation seemed necessary.

Through the kindness of the Dominion Coal Company

[1] Gmelin's Handbook, **5**, 218.

[2] Action of Air, Water, Etc., upon Cast Iron, Wrought Iron and Steel, British Assoc. Reporter, 1839 and 1841.

(Limited), several pieces of the transformed cast iron, together with pieces of wrought iron and steel, from the submerged mine, have been obtained for use at our laboratory, and, at the same time, six gallons of the mine water. From the center of a piece of transformed cast iron, a sample of the original cast iron has been obtained. In addition to the sample of cast iron just mentioned, four samples of the transformed cast iron have been selected for analysis and numbered I., II., III. and IV. for convenience. No. I. contained nothing but the light colored central part of the transformed cast iron, mentioned in the description of a cross-section of a rail; II., the outer, harder, and darker part of the piece from which I. came; III., the outside of the piece from which the gray cast iron was taken; and IV., the cross-section of a T-rail. The samples were not dried artificially, but were ground in an agate mortar, and transferred at once to glass-stoppered weighing-tubes. Analyses of these samples should disclose much of the chemical character of the transformed cast iron.

The samples have been analyzed and the calculations made by the following methods: Carbon and water have been determined by combustion with lead chromate and oxygen. In the case of the cast iron, the carbon has first been separated by the use of the double chloride of copper and ammonium.

Water mechanically held has been found by heating weighed quantities of the samples in an air-bath at 105° for four hours.

The first step in the determination of silicon and silicon dioxide in the samples, has been to oxidize the remaining silicon to silicon dioxide by fusion with sodium carbonate and potassium nitrate in a platinum crucible. The silicon dioxide resulting, has then been determined in the usual way.

Another weighed portion of the same sample, freed from water by gently heating in a porcelain boat with a small Bunsen flame, has then been transferred to a combustion furnace and treated with chlorine according to Drown's[1] method for the determination of silicon in cast iron. Afterwards the residue in the boat has been removed to a platinum crucible, mixed with sodium carbonate and potassium nitrate, and

[1] Journal of Institute of Mining Engineers, 7, 346.

fused. On cooling the fused mass has been treated in the usual way for the determination of silicon dioxide. The weight of the silicon dioxide, found in the second determination, subtracted from the weight of the silicon dioxide obtained by fusion before the treatment with chlorine, gives the weight of the silicon dioxide that has been produced by the oxidation of the silicon in the original samples. From the weight of silicon dioxide thus obtained by difference, the weight of silicon in the samples has been calculated. The weight of silicon dioxide, obtained before the treatment with chlorine, minus the weight of the silicon-dioxide, found as above by difference, gives the weight of the original silicon dioxide in the samples.

Phosphorus has been determined by the molybdate method with final precipitation as ammonium magnesium phosphate. In sample IV., which contained arsenic, the phosphorus and arsenic have been precipitated together by boiling with molybdate solution, and afterwards weighed together as magnesium pyrophosphate and magnesium pyroarseniate. In a very dilute solution of a separate portion of IV. the arsenic itself has been estimated by the use of Marsh's apparatus and standard arsenical mirrors. The arsenic has then been calculated as arsenical pyrites and magnesium pyroarseniate. The magnesium pyroarseniate subtracted from the magnesium pyrophosphate and magnesium pyroarseniate give the magnesium pyrophosphate obtained from the samples, and this has been calculated as phosphoric anhydride.

Calcium had been determined by the oxalate method; magnesium by the pyrophosphate method; and manganese by Gibbs's pyrophosphate method.

The total amount of sulphur in the samples has been determined in the usual way after fusion with sodium carbonate and potassium nitrate. The sulphur, combined with a metal or metals to form sulphide, has been determined by Blair's[1] modification of Fresenius' method. The sulphur has been calculated as ferrous sulphide. Sulphur, in the sample, above that in combination with metals to form sulphides, has been calculated as sulphur trioxide.

[1] Blair's Chem. Anal. of Iron, p. 63.

Iron has been determined by Marguerite's potassium permanganate method. Unfortunately, on account of the presence of considerable carbon and iron or less metallic iron in the samples, it has been impossible to determine the part of each sample that is ferric oxide. But this failure seems to be of little importance, since inspection of the samples alone is sufficient to show that ferric oxide is present only in small quantities, and therefore, the oxygen above that necessary to form ferrous oxide can safely be neglected.

Oxygen, above that in combination with silicon to form silicon dioxide, with hydrogen to form water, with sulphur to form sulphur trioxide, with calcium to form calcium oxide, with magnesium to form magnesium oxide, with manganese to form manganese monoxide, and with phosphorus to form phosphoric anhydride, has been determined by difference, after first assuming that the sulphide, found by direct experiment in the samples, was ferrous sulphide, and that the arsenic in IV. was combined with iron to form arsenical pyrites. If this assumption is true, it follows, for there is no carbonate in the samples, that all the oxygen in excess of that mentioned above, neglecting traces of ferric oxide, must be combined with the iron to form ferrous oxide. Therefore, to find what per cent. this oxygen is of the whole substance, it only remains to add together the percentage of each sample, that is, silicon dioxide, silicon, carbon, water, ferrous sulphide, sulphur trioxide, phosphoric anhydride, calcium oxide, magnesium oxide, manganese monoxide, arsenical pyrites, and iron above that combined with sulphur and arsenic, and to subtract the sum from one hundred. The difference, which is the percentage of oxygen in the samples above that already mentioned, has been calculated as ferrous oxide. The percentage of each sample, that is, iron combined with carbon to form carbide, FeC_2, and metallic iron, has been found by subtracting the sum of the percentages of the iron in ferrous sulphide, arsenical pyrites, and ferrous oxide from the total percentage of iron in the sample.

The analytical results below show the composition of the sample of gray cast iron and of I., II., III. and IV. These results have been calculated in per cent., and, in most cases,

are averages obtained by duplicate determinations. The specific gravities of the samples, water standard, are first given.

Gray Cast Iron.

Specific gravity 6.9.

Silicon.	Carbon.	Sulphur.	Phosphorus.	Calcium.	Magnesium.	Manganese.	Iron.	Total.
1.74	3.46	0.15	0.38	0.76	0.24	0.63	92.54	99.90

Transformed Cast Iron.

	I.	II.	III.	IV.
Specific gravity.	2.1	2.5	2.5	2.3
Silicon dioxide	17.97	12.25	10.62	27.81
Silicon	0.57	1.67	0.83	
Carbon	18.21	13.33	9.71	15.21
Water mechanically held	3.04	3.53	4.70	3.29
Water combined	5.40	5.21	7.78	4.49
Ferrous sulphide	0.33	0.38	1.25	0.96
Sulphur trioxide	1.41	2.73	3.02	0.75
Phosphoric anhydride	2.34	1.65	1.88	2.36
Calcium oxide	1.36	1.25	0.99	trace
Magnesium oxide	0.36	0.35	0.87	....
Manganese monoxide	0.30	0.30	1.90	1.84
Arsenical pyrites	....	....	....	0.68
Metallic iron + iron in the carbide FeC_2	22.84	23.06	28.55	3.37
Ferrous oxide	25.87	34.29	27.90	39.24
	100.00	100.00	100.00	100.00

On comparing the above results it is noticeable that IV. contains more silicon dioxide and less magnesium and calcium oxides than either I., II. or III. Moreover, it is not equally rich in sulphur trioxide. The thing that distinguishes IV. from the other samples more than anything else, and from the sample of cast iron is the fact that it contains arsenic. The mine water, which covered all four of the samples, contained 0.00005 gram of arsenic per liter. But, since samples I., II. and III. contained no arsenic the arsenic in IV. must have come from the cast iron, out of which IV. was produced, and not from the mine water. The cast iron, whose analysis has been given above, so far as all the analytical results obtained show, may have been the material out of which samples I. and II. have been produced, and, from the method of sampling, is

the material out of which III. has been produced; but, for reasons already given, it could not have been the material out of which IV. has been produced. Consequently the analytical results from sample IV. are not strictly comparable with those from the sample of cast iron and I., II. and III. The percentage of carbon seems large in all the samples, with the possible exception of III., even when allowance has been made for the insolubility of carbon and the loss in weight which the original cast iron has sustained. It is not large enough, however, to warrant the conclusion that the percentages of carbon in I., II., and III. have been augmented by deposition of carbon in any of these samples. It will be seen that in the production of I., II., III. and IV., considerable iron must have passed out of the original cast iron, while oxygen and water have been added. A little silicon dioxide and sulphur complete the additions which the original cast iron has received. Therefore, it would appear, from the large amount of oxygen and the comparatively small amount of other substances added, that the transformation had been brought about chiefly by the addition of oxygen. However, since the oxides of iron are insoluble in water, this supposition does not account for the loss of iron which the original castings have sustained. The iron had to be changed into a soluble compound before it could pass out into the surrounding water. An analysis of the mine water ought, therefore, to reveal the nature of this soluble compound of iron and also the solvent of the iron. I am indebted to my assistant, Mr. John W. Edwards, for a partial analysis of the Hubb mine water. The results are below.

	Grams per liter.
Free and combined sulphuric acid	0.4551
Free sulphuric acid	0.0230
Calcium	0.0419
Silicon dioxide	0.0153
Magnesium	0.0222
Chlorine	0.0284
Arsenic	0.00005
Iron, aluminium, and manganese	0.0096

On account of the presence of sulphate of iron and free sulphuric acid in considerable quantities in the mine water, the

former must have been the soluble compound of iron and the latter the solvent.

Going back to the formation of the sulphuric acid, the chemical changes in the original castings may be briefly summarized as follows: A part of the iron pyrites in the coal, acted upon by the moist air, has been converted by a well-known reaction into ferrous sulphate, free sulphuric acid, and sulphur. Once formed, the sulphuric acid has found its way into the mine water, which, after a time, has become strongly acidic enough to slowly attack the submerged cast iron. From this chemical action the sulphates of the strong metals in the castings have resulted, together with hydrogen and hydrocarbon. The soluble sulphates dissolved and passed out of the castings into the mine water, and the mixture of silicon, graphite, and the carbide of iron, FeC_3, described by Karsten, must, after a time, have resulted if the mine water had been more strongly acidic. But, instead of a strength of 10 per cent. sulphuric acid, the mine water attained only a strength of 0.0023 per cent. Consequently secondary chemical reaction set in, and the oxygen and carbon dioxide of the air, which the mine water held in solution attacked the cast iron and produced $FeO + H_2O$, $FeO_2 + FeO + H_2O$, and possibly at first a small quantity of $FeCO_3$, as described by Mallet. This reaction accounts for the existence of considerable oxide of iron in the transformed casting. The ferric iron in the compound, $Fe_2O_3 + FeO + H_2O$, could not, however, exist long in the presence of the hydrogen, produced by the action of the metallic iron on the sulphuric acid, as it would be changed to ferrous iron. The reducing action of hydrogen accounts for the almost complete absence of ferric oxide from the transformed cast iron. When taken from the mine the castings contained no carbonate. If any was ever formed, the sulphuric acid solution, after a time, became strong enough to dissolve it, with formation of ferrous sulphate, carbon dioxide and water. It is also very probable that a part of the ferrous oxide has dissolved in the sulphuric acid to form ferrous sulphate and water. Silicon and phosphorus have been gradually oxidized, while the carbon in the cast iron chemically has remained unchanged,

except for a slight loss due to the formation of hydrocarbons. Sulphuric acid and atmospheric gases, dissolved in the mine water, are the principal chemical agents that have been instrumental in changing the original castings in the Hubb mine into masses having the appearance of graphite.

TUFTS COLLEGE

Contributions from the Chemical Laboratory of the Lehigh University.

III.—THE ACTION OF SULPHURIC ACID ON ANISOL.

BY W. B. SHOBER.

Various statements have been made by different investigators concerning the result of the action of sulphuric acid on anisol (methylphenyl ether). Kekulé[1] and Cahours[2] state that when anisol is treated with sulphuric acid, para- and orthoanisolmonosulphonic acids are formed.

Annaheim[3] obtained the para and ortho acids by heating methoxysulphobenzide with sulphuric acid.

Moody[4] treated 50 grams of anisol with an equal volume of sulphuric acid at ordinary temperature. He found that the ether dissolved readily with evolution of heat. On adding the reaction-mixture to water, a portion of the anisol was liberated. This was shaken with a further quantity of sulphuric acid at 80°. The acid solution was neutralized with calcium carbonate, and the calcium salt purified by fractional crystallization. He found but *one* calcium salt. This was converted into the amide (melting-point 108°).[5] The anisol used was obtained from Kahlbaum. Moody dried it over sodium and then carefully distilled it, rejecting the first and last portions. (boiling-point 153°). Franklin[6] treated anisol, obtained by decomposing diazobenzene sulphate with methyl alcohol (boiling-point 152°–154°), with three times its weight of ordinary concentrated sulphuric acid. In one case the mixture was heated on a water-bath for two hours, in another for one hour at 80°.

[1] Ztschr. Chem., 1869, 201. [2] Ann. Chem. (Liebig), **52**, 333.

[3] *Ibid.*, **172**, 47. [4] Proc. Chem. Soc., 1892-93. 90.

[5] This melting-point is apparently too low. In this and a previous investigation, I have determined the melting-point of paramethoxybenzenesulphonamide repeatedly. Under all conditions it has melted at 112°-113°. Franklin gives the melting-point as 112°.

[6] Dissertation, 1894.

The acid mixture was poured into water and neutralized with barium carbonate. This was converted into the amide (melting-point 112°). Only *one* amide was found. Several years ago, with the object of comparing paramethoxybenzenesulphonamide obtained by decomposing paradiazobenzenesulphonic acid with methyl alcohol, and converting the resulting sulphonic acid into the amide, with the amide obtained from the sulphonic acid resulting from the action of sulphuric acid on anisol, I treated anisol with an excess of ordinary concentrated sulphuric acid.[1] The mixture was heated on the water-bath for a half hour, poured into water, neutralized with barium carbonate, and the barium salt converted into the chloride, which was found to melt at 86°. The following analysis showed the substance to be anisoldisulphon chloride:

	Calculated for $C_6H_3.OCH_3.(SO_2Cl)_2$.		Found. I.	II.
C_7 =	83.79	27.54	28.02	....
H_6 =	6.00	1.97	....	2.67
O_3 =	79.80	....	....	....
S_2 =	63.96	21.02	21.21	....
Cl_2 =	70.74	23.25	23.37	22.85

This result was unexpected, since Zervas[2], in order to make the disulphonic acid, treated anisol with fuming sulphuric acid.

The mother-liquor from which the disulphon chloride crystallized was not examined for other products. Recently I have attempted to repeat my former experiment, and, while the disulphonic acid is obtained as before, examination of the mother-liquor always shows the presence of a monosulphonic acid.

The present investigation was undertaken to determine, if possible, the conditions which influence the course of the reaction between sulphuric acid and anisol. The anisol used in the experiments described below was Kahlbaum's preparation. It was a clear, colorless liquid boiling constantly at 152°. The sulphuric acid was ordinary concentrated acid.

Experiment I.

Eighty-five grams of sulphuric acid was poured into 40

[1] This JOURNAL, 15, 388. [2] Ann. Chem. (Liebig), 103, 342.

grams of anisol. The temperature rose to 83°, and the liquid became a sherry red. The mixture was heated for 35 minutes on a rapidly boiling water-bath; a thermometer in the mixture indicated 92°.5 during the heating. After the heating the reaction-mixture, without being allowed to cool, was poured into 2 liters of water and neutralized with barium carbonate. The barium salt was converted into the sodium salt which, when dried, weighed 73 grams. This was converted into the chloride—a clear, faintly yellow oil which did not solidify on standing under water. On treatment with concentrated ammonium hydroxide it was converted into the amide, which, on crystallizing from a rather dilute solution, was obtained in the form of long, slender needles (melting-point 113°). On one occasion I obtained needles 7.5 cm. in length. The mother-liquor was carefully examined and two other amides were found. One of them melting at 169° is undoubtedly the amide of orthoanisolsulphonic acid; the other, melting at 239°, as shown by the analysis given below, is the amide of anisoldisulphonic acid. This result is not in accord with any results on record.

Weight of paramide (melting-point 113°) = 43.7 grams = 91.61 per cent.

Weight of orthoamide (melting-point 169°) = 3.7 grams = 7.76 per cent.

Weight of disulphonamide (melting-point 239°) = 0.3 grams = 0.63 per cent.

Experiment II.

This is a repetition of the experiment described by Moody.[1]

Equal volumes of the anisol and sulphuric acid (30 cc. of each; 54.6 grams acid; 29.6 grams anisol) were mixed and vigorously shaken for five minutes in a glass-stoppered cylinder. The liquid assumed a faintly pink color; the temperature rose to 52°. After standing several hours at the room temperature, the liquid was poured into a large volume of water; 1.5 cc. of anisol separated out. This was removed and the reaction-product neutralized with barium carbonate. The barium salt was converted into the sodium salt and this into the amide in

[1] *Loc. cit.*

the usual way. The dried sodium salt weighed 43 grams. Two amides were found:

Weight of paramide 10.5 grams = 87.5 per cent.

Weight of orthoamide 1.5 grams = 12.5 per cent.

This experiment confirms Kekulé's result and is at variance with that of Moody. The variation is probably due to a difference in the temperatures at which the experiments were conducted.

Experiment III.

In this experiment 1 part by weight of anisol was treated with 2 parts of sulphuric acid (14 grams anisol, 28 grams sulphuric acid), the temperature of mixing being 53°. The mixture was heated thirty minutes on a rapidly boiling water-bath. The temperature of the mixture during the heating was 92°. As above, the reaction-product was converted into the sodium salt, and this into the amide.

The dried sodium salt weighed 26 grams. Three amides were found:

Weight of paramide = 13.5 grams = 90.60 per cent.

Weight of orthoamide = 0.2 grams = 1.34 per cent.

Weight of disulphonamide = 1.2 grams = 8.06 per cent.

Experiment IV.

To determine the effect of employing a larger excess of sulphuric acid than that used in the preceding experiment, 15 grams of anisol were mixed with 60 grams of sulphuric acid, the temperature of the mixing being 61°. The mixture was heated sixty minutes on a rapidly boiling water-bath, the temperature of the mixture during the heating being 92°. The product was converted into the amide. The sodium salt weighed 35 grams. Three amides were found:

Weight of paramide = 14.0 gram = 87.5 per cent.

Weight of orthoamide = 0.4 gram = 2.5 per cent.

Weight of disulphonamide = 1.6 grams = 10.0 per cent.

In Dr. Franklin's experiments he treated 1 part of anisol with 3 parts (by weight) of sulphuric acid and heated on the water-bath for one and two hours respectively. He found but *one* amide. In Experiment III, where the proportion of acid

to anisol was 2 : 1, I found three amides, and in Experiment IV., the proportion of acid to anisol being 4 : 1, a similar result was obtained.

Experiment V.

In this experiment the proportion of acid to anisol was 6 : 1. 14 grams of anisol was treated with 84 grams sulphuric acid, the temperature of mixing being 60°. The mixture was heated thirty minutes on the water-bath, the temperature of the mixture during the heating being 92°. The reaction-product was converted into the amide. The dried sodium salt weighed 32 grams. *Two* amides were found:

Weight of paramide = 10.0 grams = 74.07 per cent.
Weight of disulphonamide = 3.5 grams = 25.93 per cent.

Experiment VI.

This is Experiment V repeated, the only difference being in the length of time of heating the mixture—sixty minutes. 14 grams of anisol and 84 grams sulphuric acid were mixed and treated as in the following experiment:

Temperature of mixing, 58°.
Time of heating, sixty minutes.
Temperature of mixture during heating, 92°.
Weight of the dry sodium salt, 33.3 grams.
Two amides were found:
Weight of paramide = 3.6 grams = 64.28 per cent.
Weight of disulphonamide = 2.0 grams = 35.72 per cent.

Experiment VII.

In this experiment the proportion of sulphuric acid to anisol was 10 : 1. 8 grams of anisol was mixed with 80 grams of sulphuric acid. The temperature of mixing was 44°. The mixture was heated thirty minutes on the water-bath, and the temperature of the mixture during the heating was 91°. As before, the reaction-product was converted into the amide. The weight of dried sodium salt obtained was 22 grams. Two amides were found:

Weight of paramide = 0.1 gram = 2.44 per cent.
Weight of disulphonamide = 4.0 grams = 97.56 per cent.

Experiment VIII.

This experiment was performed to determine the effect of a higher temperature upon the course of the reaction. 20 grams of anisol was treated with 44 grams of sulphuric acid. The mixture was heated for sixty minutes at a temperature of 120°–125°. The reaction-product was converted into the amide. The weight of dried potassium salt obtained was 40 grams. Only one amide was obtained—the paramide; the weight was 2.6 grams.

Experiment IX.

Twenty grams of anisol and 44 grams of sulphuric acid were mixed and heated for sixty minutes at a temperature of 150°–158°. The product was a thick, syrupy, reddish liquid. This was poured into water and treated as above. One amide was found, and that in very small quantity. Although the dried sodium salt weighed 49 grams, only 0.6 gram of the paramide was found.

An analysis of the amide, melting at 239°, gave the following results:

0.4429 gram substance gave 0.5242 gram of carbon dioxide and 0.1585 gram of water.

0.1681 gram substance gave 0.319 gram barium sulphate (Carius method).

1.087 gram substance gave 0.11519 gram nitrogen (Kjeldahl-Gunning method).

	Calculated for $C_6H_3.OCH_3(SO_2NH_2)_2$.		Found.
C_7	84	31.58	32.2
H_{10}	10	3.76	3.97
S_2	64	24.05	24.30
N	28	10.52	10.58
O_4	80	30.08	
	266	100.00	

The compound crystallizes in short columns of lustrous leaflets. It is difficultly soluble in cold water, soluble in hot water and in alcohol.

The anilide of paranisolmonosulphonic acid was prepared and analyzed with the following results:

0.2597 gram substance gave 0.5699 gram carbon dioxide and 0.115 gram water.

0.2144 gram substance gave 0.1886 gram barium sulphate (Carius method).

1.3685 gram substance gave 0.07166 gram nitrogen (Kjeldahl-Gunning method).

	Calculated for $C_6H_4.OCH_3.SO_2NH.C_6H_5$.		Found.
C_{13}	156	59.31	59.84
H_{13}	13	4.94	4.96
O_3	48	18.25	....
S	32	12.17	12.07
N	14	5.32	5.24
	263	99.99	

The compound crystallizes in long, fine, silky needles, melting at 109°. It is insoluble in cold water; very difficultly soluble in hot water; easily soluble in cold alcohol.

The results of the preceding experiments are herewith presented in tabular form:

Experiment.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Weight of sulphuric acid	85	54.6	28	60	84	84	80	44	44
Weight of anisol	40	28.1	14	15	14	14	10	20	20
Temperature of mixing	83°	52°	53°	61°	60°	58°	44°		
Time of heating	35		30	60	30	60	30	60	60
Temperature of heating	92.5°		92°	92°	92°	92°	91°	125°	158°
Weight of paramide	43.7	10.5	13.5	14	10	3.6	0.1	7.6	0.6
Weight of orthoamide	3.7	1.5	0.2	0.4					
Weight of disulphonamide	0.3		1.2	1.6	3.5	2.0	4.0		
Percentage of paramide	91.6	87.5	90.6	87.5	74.0	64.3	2.4	100	100
Percentage of orthoamide	7.76	12.5	1.34	2.5					
Percentage of disulphonamide	0.63		8.06	10.0	25.9	35.7	97.6		

The weights are given in grams; the time-figures in minutes.

Summary.

Anisoldisulphonic acid is formed in every case in which anisol and sulphuric acid were mixed and heated on the water-bath to 92°, the proportion of the acid increasing with the increase in the proportion of sulphuric acid, and with the increase in the time of heating.

It is not formed at a temperature of 125° or at higher temperatures.

Paranisolmonosulphonic acid was formed in every experi-

ment, the amount decreasing with increase of temperature, time of heating, and excess of sulphuric acid.

Orthoanisolmonosulphonic acid was formed in greatest quantity relatively, when anisol and sulphuric acid were allowed to react at ordinary temperatures; the large amount obtained in Experiment I was probably due to the higher temperature of mixing—83°; and to the time of heating—thirty-five minutes. It is not formed when the proportion of sulphuric acid to anisol is greater than 4 : 1.

SOUTH BETHLEHEM, PA., May 13, 1896.

REVIEWS.

THE JOURNAL OF PHYSICAL CHEMISTRY.

American chemists must experience a feeling of gratification at the appearance in this country of a journal which is to be devoted exclusively to the interests of that important branch of Physics and of Chemistry known as Physical Chemistry. Professors Bancroft and Trevor, of Cornell University, are to edit the Journal, and they evidently have settled the financial part of the problem to their satisfaction, or else they would not put the price of subscription as low as it is ($2.50 a year), nor venture to clothe the Journal so well. The first two numbers have been received, and, if the character of these is a fair criterion, the Journal is to take a high place. The titles and authors of the original articles in No. 1 are: "On Irreversible Cells," by A. E. Taylor; "Chemistry and Its Laws," by F. Wald; "On Ternary Mixtures, II," by Wilder D. Bancroft. In No. 2 are the following: "Allotropy of Sucrose," by F. G. Wiechmann; "Nascent Hydrogen," by R. Franchot; "On Irreversible Cells (concluded)," by A. E. Taylor; and "Purification of Water by Distillation," by G. A. Hulett. Besides original articles, both numbers contain book reviews and abstracts of articles on topics in the field of physical chemistry. The editors are to be congratulated on their first two numbers, and it is to be hoped that they will be able to maintain the high standard they have set. L. R.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Fortschritte des Jahres 1895. Im wissenschaftlichen Theile bearbeitet von DR. W. NERNST, o. Professor an der Universität Göttingen. Im technischen Theile bearbeitet von DR. W. BORCHERS, Lehrer an der Kgl. Maschinenbau und Hüttenschule, zu Duisburg. II Jahrgang. Wilhelm Knapp. Halle, A. S. 1896. pp. 300.

Although the appearance of the first volume of the *Jahr-*

buch der Elektrochemie has already received notice in this Journal,[1] the second volume seems to call for special comment. The most striking feature of this work is the relative importance which technical electrochemistry has acquired. Of the three hundred pages contained in the book, only thirty-six are devoted to a review of the scientific development of electrochemistry during the year which the volume covers.

The reviews of technical operations and processes are in many cases fairly elaborate, and fortunately so, since many pieces of work in this line are published in places which are more or less inaccessible to the average reader, or are covered by patents, and would be overlooked by him.

Of especial interest are the chapters on accumulators, and the new devices for obtaining high temperatures by means of the current itself. The work of Moissan on the artificial preparation of the diamond is mentioned, but very briefly. His investigations which led to the liberation of several of the elements from their compounds, by means of the current, are considered at greater length.

We find here an account of the improvements in the metallurgical processes for separating sodium, potassium, magnesium, glucinum, aluminium, silver, gold, copper, zinc, tin, nickel, cobalt, chromium, molybdenum and iron. In the chapter on those interesting compounds, the carbides, it is stated that the cost of obtaining calcium carbide is about ninety-seven marks per thousand kilograms.

This has, of course, an important bearing upon the use of acetylene as an illuminant.

This volume, like the first, contains an unusual number of cuts of apparatus. Indeed one hundred and ninety-seven are employed to illustrate the text.

It is to be hoped that so commendable a work will receive the support which it deserves. H. C. J.

FOODS; THEIR COMPOSITION AND ANALYSIS. BY ALEXANDER WYNTER BLYTH, M.R.C.S., F.I.C., F.C.S., etc. 7th Edition. London: Charles Griffin & Co. New York: D. Van Nostrand Co.

Part I. of this book is mainly historical. It treats of the practice and the punishment of adulteration in earlier times, more particularly in England, France, and Germany, and gives an account of English legislation with regard to the adulteration of food, and also of the development of the processes for its detection. Part II. deals with some of the forms of apparatus useful in food analysis, the application of the microscope, the spectroscope and photography to the chemis-

[1] This JOURNAL, 18, 262.

try of foods, and the analysis of ash and estimation of nitrogen. The remaining parts, III.–IX., are special, treating of carbohydrates, including the cereals; products of the dairy; tea, coffee and cocoa; alcoholic liquors; vinegar; condiments; and water.

The work, though it lacks the exhaustive character of Koenig's *Nahrungs- und Genussmittel*, is one of great merit. It will be especially welcome to those who wish to obtain a correct and adequate view of the status, in England, of the problem of food adulteration and its suppression. H. N. M

THE ELEMENTS OF ELECTROCHEMISTRY. By MAX LE BLANC, Professor of Chemistry in the University of Leipsic. Translated by W. R. WHITNEY, Instructor of Chemistry in the Massachusetts Institute of Technology, of Boston, U. S. A. Macmillan & Co., London and New York. 1896. pp. 284.

The English translation of this excellent work by Le Blanc, the original of which has already been noticed in this JOURNAL,[1] will be welcomed by American and English students of electrochemistry. It is especially opportune, since it is the first book in English which deals with the modern developments of electrochemistry in a comprehensive manner. The reviewer is not unmindful of the volume on "Solutions and Electrolysis," by Whetham, which contains several valuable chapters on the electrical properties of solutions; but, as is implied in the title, only that side of electrochemistry is treated which has to do more directly with solutions.

The point is often made that it is better to read the original than a translation, and this is true, where the reader possesses sufficient knowledge of the foreign tongue. But the fact remains that a student of physical chemistry, who has not worked in Germany, will reach the stage at which he can read an advanced work on electrochemistry, intelligently, before he has acquired a knowledge of the German language which will enable him to use it unconsciously. Further, to grasp the subject of electrochemistry is not a simple task, and when the student must divide his energy between the contents of the book and the language in which it is written, the result is not likely to be entirely successful. For these and other reasons the translation of such a book as this meets a want, and the time of the translator has been well spent.

A comparison with the original will show that Dr. Whitney has furnished us with a satisfactory translation. This is further insured by the fact that the proof has been read by Dr. A. A. Noyes. H. C. J.

[1] This JOURNAL, 18, 521.